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Vapor Signatures from Military Explosives

Part 1. Vapor Transport from Buried Military-Grade TNT

Thomas F. Jenkins, Daniel C. Leggett,
and Thomas A. Ranney

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Abstract: Crystals of military-grade TNT were placed beneath 2.5 cm of soil in enclosed 40-mL amber vials and the accumulation of signature vapors in the headspace above the soil was determined as a function of time. Three different soils—sand, silt, and clay—were investigated at three different moisture contents: air dry, low moisture, and high moisture. Two replicates of each combination of soil type and soil moisture were equilibrated at three temperatures (23, 4 and –12°C) over periods ranging from 63 to 173 days.

The headspace was sampled by a polyacrylate solid phase microextraction (SPME) fiber for periods ranging from 5 to 20 minutes, and analytes were desorbed in the injection port of a gas chromatograph equipped with an electron capture detector. Mass detection limits using this method were below 1 pg (1×10^{-12} g) for the major signature chemicals—2,4-dinitrotoluene (2,4-DNT), 1,3-dinitrobenzene (1,3-DNB), and 2,4,6-trinitrotoluene (2,4,6-TNT). At the end of the experiment, the top 5 mm of soil was carefully removed, extracted with acetonitrile, and the extracts were analyzed using RP-HPLC-UV according to SW846 Method 8330.

Both the qualitative and quantitative nature of the chemical signature above buried TNT is strongly a function of temperature. At 23 and 4°C, 2,4-DNT was present at the highest concentration in the headspace vapor, 2,4,6-TNT being only a minor component. At –12°C, the more volatile 1,3-DNB predominated. Vapors penetrate the soils in the order sand > silt > clay, with vapor concentrations in the same order. Dry soils are very retentive of TNT vapors, while soil moisture facilitates movement of vapors to the headspace.

Soil–air partition coefficients, computed for these three soils at 23 and 4°C for 2,4,6-TNT, ranged from 1.6×10^4 mL-air/g-soil for moist sand at 23°C to 3.0×10^7 for moist clay at 4°C. Partition coefficients for 2,4-DNT were about an order of magnitude lower. Vapor concentrations for several of the air-dried soils were too low to measure and hence the partition coefficients for dry soils could not be estimated, but were much higher than for the same soil with higher moisture. These results indicate that for detection of buried mines, the largest mass of signature chemicals will be present in the surface soil rather than the overlying air.

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OFFICE OF THE CHIEF OF ENGINEERS

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PREFACE

This report was prepared by Dr. Thomas F. Jenkins, Research Chemist, Geological Sciences Division, Daniel C. Leggett, Research Chemist, Geochemical Sciences Division, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, and Thomas A. Ranney, Staff Scientist, Science and Technology Corporation, Hanover, New Hampshire.

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Part 1. Vapor Transport from Buried Military-Grade TNT

THOMAS F. JENKINS, DANIEL C. LEGGETT, AND THOMAS. A. RANNEY

INTRODUCTION

Background

In the early 1970s, CRREL personnel conducted a series of experiments for which the ultimate goal was to define the vapor signatures of buried landmines. The strategy employed was to initially define the signature of military-grade explosives and then try to understand the attenuation and modification of these signatures attributable to the mine casings and soil barriers. The intent was to provide this information to those groups that were developing chemical sensors to detect the presence of landmines by sensing their associated vapor signature in near-real time.

Initially, the vapor signature of military-grade TNT was investigated. Using gas chromatography with an electron capture detector (GC-ECD), Murrmann et al. (1971) found that while 2,4,6-trinitrotoluene accounted for 99.8% of the solid military-grade TNT sample they studied, it provided only 58% of the equilibrium vapor in the headspace above the solid TNT. The manufacturing impurity, 2,4-dinitrotoluene (2,4-DNT), while accounting for only 0.08% of the solid explosive, accounted for 35% of the vapor composition owing to its much higher vapor pressure. The remainder of the vapor composition was other isomers of DNT and TNT. The authors concluded that 2,4-DNT could be as important as 2,4,6-TNT for purposes of land mine detection. Despite a special effort to detect vapor components other than isomers of TNT and DNT using GC-ECD and GC-flame ionization detection (GC-FID), no other vapor components were identified.

In a more detailed study, Leggett et al. (1977) reported results for 8 domestic and 14 foreign military-grade TNT samples. Except for two unknown compounds that responded on the GC-ECD, the results confirmed that the major portion of the vapor composition was ascribable to the various isomers of DNT and TNT. The largest component of the vapor was 2,4-DNT for all eight domestic TNTs, and all but four of the foreign TNTs. In most cases, the concentration of 2,4-DNT in the vapor exceeded that for 2,4,6-TNT by an order of magnitude or more.

A preliminary study was also conducted to assess how quickly vapors of military-grade TNT could penetrate soil barriers (Jenkins et al. 1974). In this study, 1 g of military-grade TNT was placed on top of portions of two moist test soils (a sand and a clay) and was then covered with 2.5 cm of the appropriate soil in enclosed septum vials. The vials were stored at room temperature for 25 days and the headspace above the soil was sampled periodically. The results indicated that 2,4-DNT had penetrated through the soil to the headspace within 4 days, while vapors of 2,4,6-TNT were not detectable in the headspace until day 12 (Table 1). From these results, the authors concluded that DNT and TNT vapors can diffuse through soil barriers in a relatively short period, and during the diffusion process, vapors are largely retained within the soil barrier (Table 2). Therefore, the surface soil directly above a buried mine should have considerably larger amounts of DNT and TNT than the headspace above.

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Table 1. Concentration (g/mL) of 2,4-DNT and 2,4,6-TNT in the headspace. (After Jenkins et al. 1974.)

	Ft. Belvoir clay		*Windsor sand*	
Day	*2,4-DNT*	*2,4,6-TNT*	*2,4-DNT*	*2,4,6-TNT*
0	<d*	<d	<d	<d
4	1.2×10^{-12}	<d	t†	<d
6	5.0×10^{-12}	<d	t	<d
7	1.4×10^{-11}	<d	1.8×10^{-12}	<d
10	N.D.**	N.D.	2.1×10^{-12}	<d
12	3.1×10^{-11}	t	2.8×10^{-12}	t
13	N.D.	N.D.	1.3×10^{-11}	t
14	N.D.	N.D.	1.4×10^{-11}	t
18	N.D.	N.D.	1.6×10^{-11}	t
19	8.0×10^{-11}	5.8×10^{-13}	N.D.	N.D.
25	N.D.	N.D.	2.6×10^{-11}	7.0×10^{-13}

* Concentration was less than an estimated detection limit of about 1×10^{-13} g/mL.
† Trace.
** No data.

Table 2. Analysis of a soil cover (Ft. Belvoir clay) for DNT and TNT content. (After Jenkins et al. 1974.)

Analyte	*Concentration in g/g of soil*
2,6-DNT	6.2×10^{-6}
2,5-DNT	8.0×10^{-6}
2,4-DNT	1.4×10^{-4}
2,4,6-TNT	9.3×10^{-5}

Objective

Our major objective was to conduct a more detailed experiment to investigate the qualitative and quantitative effects of soil barriers at various temperatures on the vapor signature from buried military-grade TNT.

The overall strategy for this study was to set up small-scale experiments where we buried a small quantity of military-grade TNT beneath soil in an enclosed container and to analyze the headspace vapor periodically to determine the rate of breakthrough of the various explosives-related vapors.

Experiments were conducted to assess the effects of soil type, moisture content, and ambient temperature on the rate of breakthrough and the qualitative and quantitative nature of the vapor signatures. At the end of the experiments, the surface soil was sampled to relate the vapor signature in the headspace to the explosives-related signature present in the surface soil.

EXPERIMENTAL METHODS

Soils used for experiment

Three soils were selected for this study because of their textural differences. A natural silica sand from Ottawa, Illinois (ASTM 1999), was selected to represent coarse-grained material with little or no organic carbon content. This material was used as received. The second soil selected was Hitchcock silt loam, which is a native soil at our location, and represents a medium-textured soil. The third soil selected, Fort Edward clay, represents a fine-grained material. Both the silt loam and clay soils were passed through a no. 40 sieve (420 µm) to remove some of the larger stable aggregates. The approximate grain size distribution for these soils is presented in Table 3.

The three soils were each studied at three different moisture levels: air dry, low moisture, and high moisture (Table 3). To moisten the soils, a layer of each was spread out in a large aluminum pan and wetted with well water (from a deep residential water well in Hartland, Vermont) using a hand pump sprayer. The pan was shaken to mix the soil and more water was added. This procedure was continued until the approximate desired moisture level was obtained. This process was duplicated with a new soil sample and an additional amount of water was added to raise the soil to a higher moisture level. The final moisture content of the soils was determined by weighing two subsamples of each moist soil, allowing them to air dry, then weighing again, and obtaining the moisture by difference.

Table 3. Physical characteristics of soils used in explosives vapor transport study.

	Approximate grain size distribution (%)			*Moisture based on wet weight (%)*		*Bulk density (g/cm^3)*		
Soil	*Sand*	*Silt*	*Clay*	*Low level*	*High level*	*Air dry*	*Low moisture*	*High moisture*
Ottawa sand	100			2.1	3.1	1.65	1.58	1.64
Hitchcock silt	18	73	9	5.8	10	1.14	1.25	1.28
Fort Edwards clay	5	11	84	15	33	1.09	1.11	1.29

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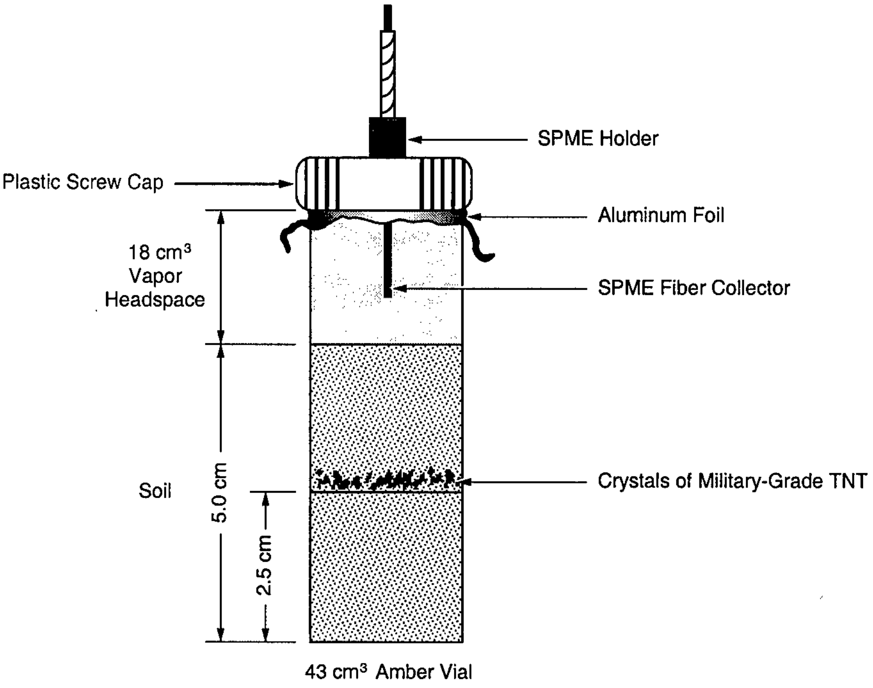

Figure 1. Soil test device.

Design of experiment

Replicates of each air-dried soil and each of the two higher moisture level soils were placed in 40-mL , 27- × 95-mm amber vials (six replicates of each) to a depth of 2.5 cm. We used 40-mL (43 mL total capacity) amber vials (Krackler Scientific) with open-top screw caps, septa removed, throughout the study. The vials were rinsed with acetone and oven dried at 105°C for several hours prior to being used. We compacted the soil in each vial by dropping it several times onto a padded counter from a height of 5 cm. Previously ground and weighed (110-mg) portions of military-grade TNT from Picatinny Arsenal were placed on top of the soil using a long-stemmed polyethylene funnel. The TNT was spread into a disk shape approximately 13 mm in diameter and 1 mm deep, centered in the vial. Care was taken to be sure no TNT touched the vial walls. An additional 2.5 cm of soil was then carefully placed in the vial, covering the TNT, and the soil was compacted as previously described. Bulk densities of the soils were determined by weighing two representative vials of each soil, at each moisture level (Table 3). The vial weight was subtracted and the resulting soil weight was divided by the volume occupied by the 5 cm of soil (25 cm^3). Commercially available aluminum foil covered the vial opening and was secured in place using a plastic screw cap (Fig. 1). Two replicates for each combination of soil type and moisture level (18 vials) were stored at room temperature (23°C), at 4°C, or at −12°C. All vials were wrapped with a sheet of aluminum foil to eliminate photocatalyzed reactions. Headspace samples were collected using solid phase microextraction (SPME) fibers at a number of time intervals from 11 to 173 days as described below. After 63 days, we opened some replicates following headspace sampling, and sampled and analyzed the surface soil for explosives-related compounds as described below. Other replicates were treated in an identical manner at periods up to 173 days.

Soil sample collection, solvent extraction, and analysis using RP-HPLC

After conducting the 63-day vapor analysis, we decided to begin sampling the top 5 mm of soil in one of the replicate vials (A) of the samples stored at room temperature (23°C). We did a similar sampling on the 4°C samples after 67 days and on the −12°C samples after 69 days. Soils were sampled for replicate A, regardless of whether or not signature chemicals were detectable in the vapor. The remaining replicate samples (B) continued their usual storage, with periodic analysis of the

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headspace. When analysis indicated significant analyte in the headspace vapor, the top 5 mm of soil in the B replicate samples was removed as above. After 173 days, the final remaining soils (−12°C) were sampled.

To conduct the soil sampling, we opened the vials and used a small scoop to carefully remove the top 5 mm of soil. The mass of soil removed varied from about 2 to 4 g. The soil was transferred to a 20-mL scintillation vial and a 10.0-mL aliquot of acetonitrile added. The vials were placed in a room-temperature, controlled, ultrasonic bath and extracted for 18 hours as described in SW 846 Method 8330 (EPA 1995).

Table 4. Retention times* for explosives-related compounds by RP-HPLC.

Analyte	*Retention time (min)*	*Analyte*	*Retention time (min)*
1,3,5-TNB	2.51	3,5-DNT	11.11
1,4-DNB	3.88	2,6-DNT	13.61
1,3-DNB	4.93	3,4-DNT	13.86
2,4,6-TNT	5.66	2,3,6-TNT	14.13
1,2-DNB	7.07	2-ADNT	14.56
3,5-DNA	7.84	3,4,5-TNT	16.56
2,4,5-TNT	8.75	4-ADNT	16.87
2,5-DNT	9.89	2,3-DNT	18.75
2,3,5-TNT	10.80	2,3,4-TNT	40.54
2,4-DNT	11.05		

*Analysis conducted on a 15-cm × 0.39-cm, 4-µm film, LC-8 column (Waters Nova-Pak) maintained at 28°C and eluted with 15/85 (V/V) isopropanol/water at a flow rate of 1.4-mL/min.

Analyte concentrations in the soil extracts were determined by reversed-phase high-performance liquid chromatography (RP-HPLC). A modular system was employed, consisting of a Dynatech LC-241 autosampler with a 100-µL injection loop, a Spectra Physics SP8810 isocratic pump, a Spectra Physics SP100 variable-wavelength UV-detector set at 254 nm, and a Hewlett Packard 3396 series II digital integrator. Separations were obtained on a 15- × 0.39-cm, 4-µm film, LC-8 column (Waters Nova-Pak) maintained at 28°C and eluted with 15/85 (V/V) isopropanol/water at a flow rate of 1.4-mL/min. The detector response was obtained from the digital integrator operating in the peak height mode. For both RP-HPLC analysis and gas chromatography with a microelectron capture detector (GC-µECD), standard analytical reference materials (SARMs) were used in making the standard solutions in HPLC grade acetonitrile (Sigma-Aldrich). Retention times for the various explosives-related analytes are presented in Table 4. Additional confirmation of analyte identities was obtained by analyzing several of the 63-day replicate A sample extracts on a 25-cm × 4.6-mm (5-µm) LC-18 (Supelco) column eluted with 50:50 methanol/water at 1.5 mL/min.

Vapor sampling using SPME and vapor analysis using GC-µECD

The headspace vapor was sampled by solid phase microextraction (SPME) using an 85-µm film coating of polyacrylate on a fused silica fiber (Supelco) (Fig. 2). We conditioned the fiber before use following the manufacturer's recommendations. Also, at the beginning of each sampling

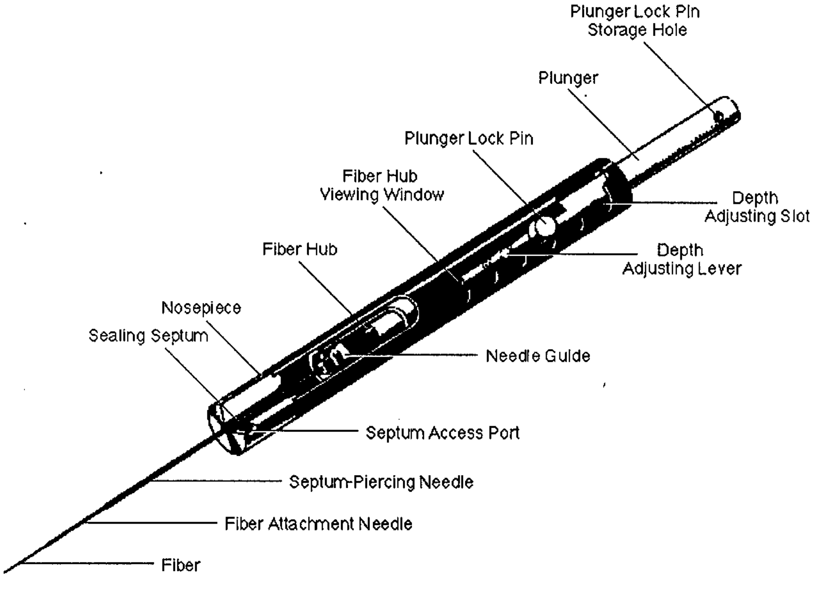

Figure 2. Portable solid-phase microextraction (SPME) field sampler (Supelco).

Table 5. Retention times for explosives-related compounds by gas chromatography.

	Retention time (min)			*Retention time (min)*	
Analyte	*DB-1 column*	*RTX-200*	*Analyte*	*DB-1 column*	*RTX-200*
1,4-DNB	3.97	7.76	2,4,6-TNT	7.01	11.37
1,3-DNB	4.23	8.16	2,3,6-TNT	7.13	11.37
1,2-DNB	4.41	8.71	2,3,5-TNT	7.54	12.17
2,6-DNT	4.44	7.83	2,4,5-TNT	7.78	12.53
2,5-DNT	4.89	8.43	2,3,4-TNT	7.98	12.93
2,3-DNT	5.18	9.22	RDX	8.07	13.38
2,4-DNT	5.28	9.05	3,4,5-TNT	8.62	13.87
3,5-DNT	5.50	9.46	4-ADNT	9.14	12.54
3,4-DNT	5.79	10.25	3,5-DNA	9.24	13.00
1,3,5-TNB	6.61	11.52	2-ADNT	9.59	13.38

* The capillary column was a DB-1, 6 m × 0.53 mm i.d., 1.5 µm. Operating parameters were: initial column temperature of 100°C (hold 2 min), ramp to 200°C at 10°C/min, then 20°C/min to 250°C and hold for 5 min. The injection port and detector temperatures were 250°C and 300°C, respectively. The carrier gas was hydrogen with a constant flow rate of 12 mL/min. Analyte identities were confirmed by analyzing a number of SPME samples on an RTX-200 capillary column, 6 m × 0.53 mm i.d. using hydrogen carrier at 10 mL/min.

event, the fiber was thermally desorbed in the injection port of the gas chromatograph (250°C) to assure that it was clean. To sample the headspace, the aluminum foil was punctured by the needle housing of the fiber and the fiber was extended into the headspace for a sorption period of 20 minutes. The opening in the screw cap was just the size of the outer diameter of the SPME holder and helped hold the assembly during sampling. Later in the study, this sampling time was reduced because the concentration of some analytes in the headspace increased to the point where the amount collected over the 20-minute sampling period maximized the detector signal.

After the sampling was complete, the fiber was withdrawn into its protective needle and the needle was removed from the vial. The outside of the needle was wiped with a tissue wetted with acetonitrile to eliminate any vapors sorbed to the metal and inserted into the injection port of the gas chromatograph. The GC-system consisted of an HP 6890 gas chromatograph equipped with a micro-electron capture detector (µECD). The capillary column was a DB-1, 6 m × 0.53 mm i.d., 1.5 µm. Operating parameters were: initial column temperature of 100°C (hold 2 minutes), ramp to 200°C at 10°C/min, then 20°C/min to 250°C and hold for 5 minutes. The injection port and detector temperatures were 250 and 300°C, respectively. The carrier gas was hydrogen with a constant flow rate of 12 mL/min. Retention times for the target analytes are presented in Table 5.

Analyte identities were confirmed by analyzing a number of SPME samples on an RTX-200 capillary column, 6 m × 0.53 mm i.d.; the carrier gas was hydrogen at 10 mL/min (Table 5). It should be noted that whenever SPME fibers containing TNT were desorbed into the hydrogen carrier gas and separated on either the DB-1 or the RTX-200 columns, we observed peaks ascribable to 2ADNT and 4ADNT (2-amino-4,6-dinitrotoluene and 4-amino-2,6-dinitrotoluene). Subsequent research revealed that these transformation products of TNT were being produced by reduction of TNT by the hydrogen carrier, presumably because of catalysis on the hot metal protective needle of the SPME device. These amino reduction products were eliminated when the carrier gas was changed to helium.

RESULTS AND DISCUSSION

Qualitative nature of headspace signatures

The signature chemicals observed in the headspace samples above military-grade TNT were: 1,2- and 1,3-dinitrobenzene (DNB), 1,3,5-trinitrobenzene (TNB), the various isomers of dinitrotoluene (DNT), and 2,3,6- and 2,4,6-trinitrotoluene (TNT). 2ADNT and 4ADNT were also observed, but, as mentioned above, we subsequently determined that these two compounds were being formed by reduction of 2,4,6-TNT in the presence of the hydrogen carrier gas in the injector of the gas chromatograph (GC). We did

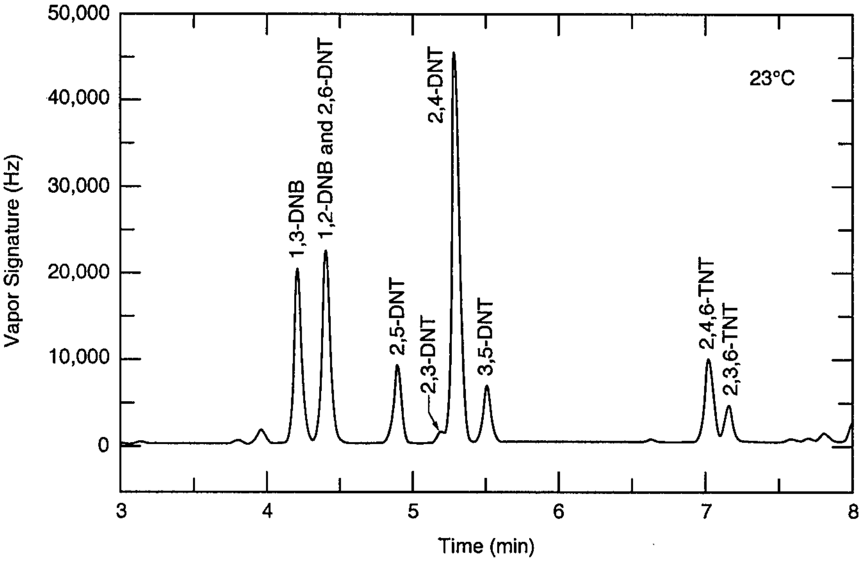

Figure 3. Vapor signature of 1966 military-grade TNT.

not observe this phenomenon when standards of TNT in acetonitrile were injected into the GC, and we postulate that the metal housing surrounding the SPME fiber catalyzed this reduction in the presence of hydrogen in the injection port. When helium was substituted for hydrogen as the carrier gas, the two peaks corresponding to these compounds disappeared. For samples where 2ADNT and 4ADNT were measured, the concentration values were stoichiometrically converted to, and added to, the TNT concentration.

An example GC-μECD chromatogram of the equilibrium vapor above military-grade TNT (Picatinny Arsenal, 1966 vintage), sampled with a polyacrylate SPME fiber for 3 minutes, is presented in Figure 3. The major peaks correspond to 2,4-DNT, 1,3-DNB, 1,2-DNB, 2,3,6-TNT, and 2,4,6-TNT, and several other isomers of DNT. These results are consistent with those presented by Murrmann et al. (1971) and Leggett et al. (1977) for vapors from various samples of military-grade TNT. Several of the early eluting peaks that were reported as unknowns by Leggett et al. (1977) were probably 1,2-DNB and 1,3-DNB.

The qualitative nature of the vapor signature in the headspace above the buried TNT is modified substantially from the equilibrium vapor above TNT. Figure 4 presents the GC-μECD chromatogram for the SPME fiber (polyacrylate) sample of the headspace vapor above TNT that was buried in Ottawa sand for 35 days at 4°C. The most obvious difference between the vapor collected over the buried TNT and that from equilibrium TNT vapor is the reduction in the peaks corresponding to 2,4,6-TNT and 2,3,6-TNT above the buried TNT, relative to the peak for 2,4-DNT and those corresponding to the isomers of DNB. The differences in absolute responses in Figures 3 and 4 are not meaningful

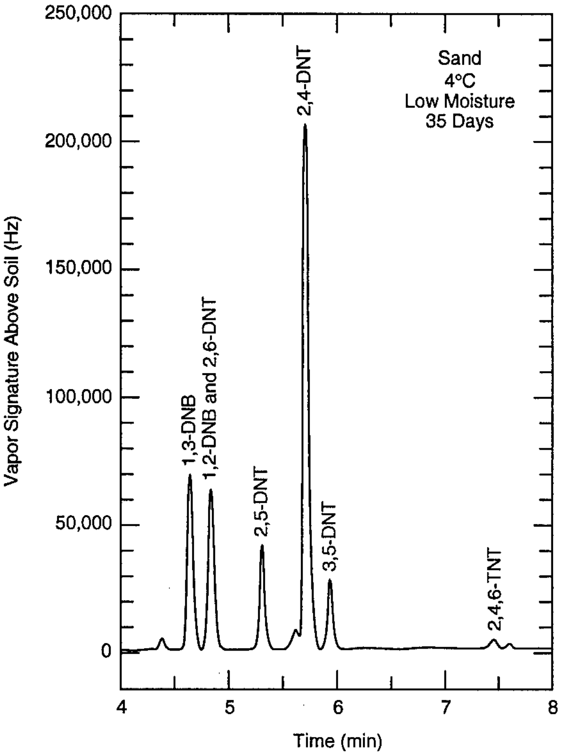

Figure 4. Vapor signature above low-moisture sand held at 4°C for 35 days.

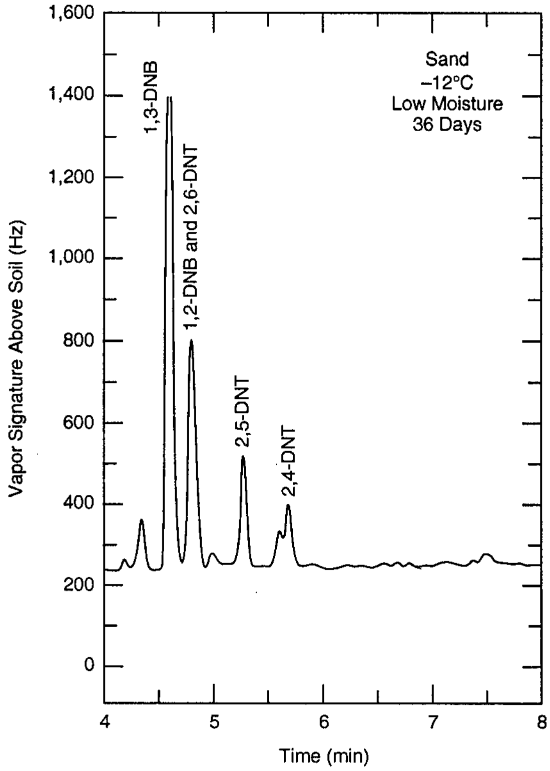

Figure 5. Vapor signature above low-moisture sand held at −12°C for 36 days.

because these two samples involved different exposure periods for the SPME fibers.

Figure 5 presents the GC-μECD chromatogram from the SPME fiber corresponding to the headspace vapor above TNT buried in Ottawa sand for 36 days, but held at −12°C. In this case, the peaks corresponding to the TNT isomers are no longer visible, and even the peak corresponding to 2,4-DNT, the most abundant peak at 4°C, is reduced relative to those for the more volatile isomers of DNB. Thus, soil temperature is an important factor in the modification of the qualitative nature of the vapor signatures above buried military-grade TNT.

Table 6 shows the effects of soil type and moisture content on headspace vapors. Concentrations of the various nitroaromatics are about an order of magnitude higher over sand than silt and about two orders of magnitude higher than over the clay. Large differences are also apparent between moist and air-dried soil, regardless of soil type. Generally, the vapor concentrations over moist soils are an order of magnitude or more higher than over air-dried soils. The headspace concentrations were similar, though, for the mid- and high-moisture levels for all three soils.

Overall, these results demonstrate that the qualitative nature of the vapor signature above buried military-grade TNT depends on the environmental conditions present in the soil, namely soil temperature, soil type, and soil moisture content.

Calibration of SPME fibers for quantification of analytes in headspace samples

SPME fibers were used in this study because of their ability to provide an enormous preconcentration of explosives-related vapors, and to efficiently transfer these collected vapors to the injection port of a gas chromatograph. This preconcentration is necessary because the concentration of headspace vapors above buried military-grade TNT is expected to be very low. For example, Jenkins et al. (1974) measured concentrations of TNT in headspace vapors above buried TNT in the range of 10^{-11} to 10^{-13} g/mL. While the μECD detector is very sensitive and can detect less than

Table 6. Analyte mass (pg) collected in 1 minute from headspace vapor using SPME above soils containing buried U.S. military-grade TNT, at 23°C, and three moisture levels after 6 days of equilibrium.

Soil	*Rep A*	*Rep B*	*Rep A*	*Rep B*	*Rep A*	*Rep B*
Sand	**Air dry**		**2.1% moisture**		**3.1% moisture**	
1,3-DNB	29.3	41.2	561	433	285	289
1,2-DNB	16.5	21.1	106	79.2	57.9	59.8
2,5-DNT	2.34	<d*	61.6	<d	35.9	37.9
2,4-DNT	2.36	3.93	754	600	441	497
3,5-DNT	<d	d	175	<d	108	119
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	0.267	0.305	20.8	14.9	13.7	32.8
Silt	**Air dry**		**5.8% moisture**		**10% moisture**	
1,3-DNB	<d	<d	59.4	64.9	49.7	51.4
1,2-DNB	<d	<d	8.80	50.5	8.40	8.44
2,5-DNT	<d	<d	2.50	15.6	1.91	1.85
2,4-DNT	0.145	0.274	49.7	131	51.4	51.3
3,5-DNT	<d	<d	15.8	27.2	15.4	15.0
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	0.652	0.807	1.59	1.71	1.54	1.83
Clay	**Air dry**		**15% moisture**		**30% moisture**	
1,3-DNB	<d	<d	2.34	2.24	2.29	1.64
1,2-DNB	<d	<d	1.19	1.31	1.22	1.00
2,5-DNT	<d	<d	<d	0.054	<d	<d
2,4-DNT	<d	<d	<d	<d	<d	<d
3,5-DNT	<d	<d	†	†	†	†
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	<d	<d	<d	<d	<d

* Below detection level.

† An interference precluded determination of 3,5-DNT in these samples.

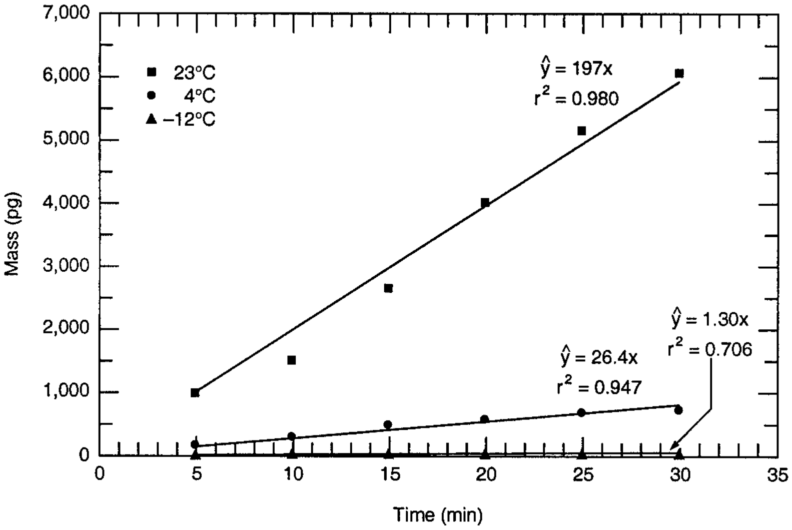

Figure 6. Mass of TNT vapor collected on polyacrylate SPME fiber at different temperatures.

10^{-12} g of TNT, it would require air sample volumes of 10 mL or so to deliver a detectable mass of TNT to the GC if the vapor concentration was 10^{-13} g/mL; direct injection of that volume of air containing semi-volatile organics with very low vapor pressures is difficult to achieve without losses.

The major difficulty with the use of the SPME fibers for this application is the difficulty of providing quantitative calibration. Instrument responses for explosives vapors obtained by SPME can easily be calibrated with respect to mass. Using liquid standards to obtain response factors, we can convert to mass of TNT a peak height (or peak area) for TNT in the GC-μECD chromatogram from a sample preconcentrated on a SPME fiber. However, to convert this mass to a vapor concentration in the headspace, the volume sampled by the fiber needs to be known.

Previous approaches to calibration for SPME assume that equilibrium is reached between the fiber and the vapor (Zhang and Pawliszyn 1993, Martos and Pawliszyn 1998). Experiments at Sandia National Laboratory* and here at CRREL indicate that equilibrium for TNT is not reached even when the headspace is exposed to the fiber for several days. One exception is the dimethysiloxane SPME fiber with only a 7-μm coating. In that case, equilibrium appears to be reached more quickly (order of minutes to hours), but little preconcentration is achieved. This has been verified at both CRREL and Sandia.

In an early experiment, we examined the relationship between mass of TNT collected and the length of time the fiber was exposed to the equilibrium vapor above military-grade TNT. This was done by placing 28 mg of U.S. military-grade TNT in a 40-mL amber vial and allowing it to equilibrate for 3 days at room temperature. A polyacrylate SPME fiber (85 μm) was inserted into the vial and was exposed to the vapor for periods ranging from 5 to 30 minutes. This was done at all three temperatures used in the soil study: 23, 4, and −12°C. A plot of the mass of TNT collected as a function of exposure time for each temperature is shown in Figure 6. The results indicate that the mass of TNT collected is linearly related to exposure time through 30 minutes for all three temperatures. In this experiment, there was a 20-minute recovery period between exposure periods, and in order for linearity to be maintained over the entire experiment, this recovery period must have been adequate to reestablish equilibrium between the TNT in the vapor and the solid.

Because the mass of TNT collected by the fiber is linearly related to exposure time, the TNT in the vapor cannot be depleted substantially in the vapor during sampling. To directly assess the rate at which TNT in the vapor could be depleted using the SPME fibers, the following experiment was conducted. An 80-mg portion of U.S. military-grade TNT was placed in a 40-mL amber vial and the headspace was allowed to equilibrate for 7 days at 23°C. The headspace in the vial was then sampled using polyacrylate SPME fibers continuously for 200 minutes in 20-minute increments.

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* Personal communication with William Chambers, Sandia National Laboratory, 1998.

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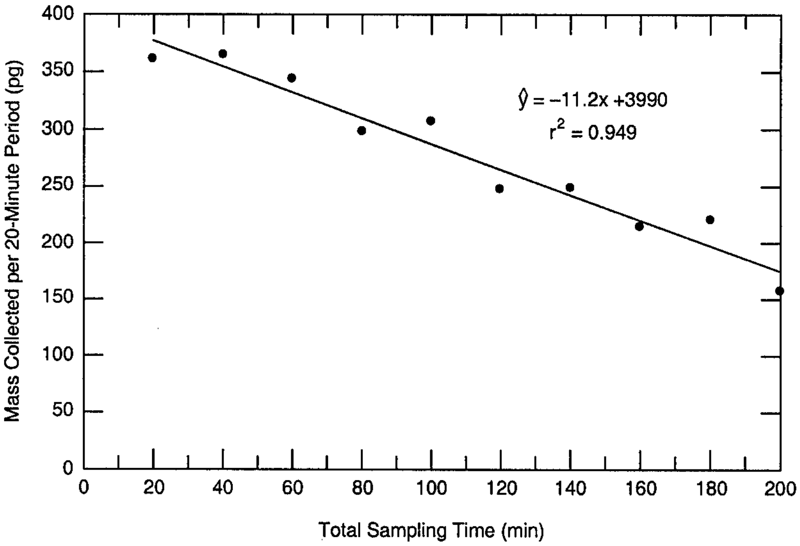

Figure 7. Continuous sampling of TNT vapor by alternating two polyacrylate SPME fibers at 20-minute intervals.

Two fibers were used, so that while one fiber was sampling the headspace in the vial, the other was being desorbed and the sample analyzed by GC-μECD.

The results for TNT are shown in Figure 7. While there was a slight difference in the mass of TNT sorbed by one of the fibers compared to the other, the general trend was a decreasing recovery with exposure time. In this experiment, there was no recovery time between sampling periods to allow reestablishment of equilibrium, and the TNT in the vapor was being sorbed by the fiber faster than it could be replaced from the solid TNT source. The rate of depletion was slow, however. For example, using the slope obtained from the best fit of the data to a linear depletion model, the mass of TNT sorbed in the first 20-minute exposure period was about 3.77 ng, while that sorbed in the second period was 3.54 ng. This was only a 6% reduction, even without a recovery period between exposure periods. Thus, when only a single 20-minute exposure period is used, the depletion of the TNT in the vapor is insignificant over the exposure period, and for practical purposes, the vapor concentration can be considered to be constant during sample collection.

Sorption of TNT by the polyacrylate SPME fiber can be thought of as follows:

$$\text{TNT (vapor)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{TNT (fiber surface)}$$

$$\overset{k_2}{\rightleftharpoons} \text{TNT (fiber bulk).}$$

The rate of surface sorption of TNT on the fiber (k_1) and the rate of desorption back to the vapor (k_{-1}) is probably fast compared with the rate of diffusion of TNT from the surface of the fiber into the bulk phase (k_2), since vapor diffusion is many orders of magnitude greater than diffusion in a condensed phase. In the case where TNT in the vapor is being replaced by sublimation from the crystal, the following equation is relevant.

$$\text{TNT (crystal)} \overset{k_3}{\rightleftharpoons} \text{TNT (vapor)}$$

$$\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{TNT (fiber surface)}$$

$$\overset{k_2}{\rightleftharpoons} \text{TNT (fiber bulk).}$$

Since the mass of TNT collected in subsequent exposure periods declines slowly (Fig. 7), the rate of k_3 must be slightly slower than the rate of diffusion of TNT from the fiber surface into the bulk of the fiber (k_2). For our soil experiment, though, we do not envision that TNT that has migrated from the buried crystals to the surface is present as crystalline TNT, but rather as TNT sorbed to soil particles. The rate of replacement in the vapor by desorption from the soil particles is likely to be different from the rate of sublimation from crystalline TNT.

To evaluate the effect of this on the use of the SPME fibers to sample the headspace above soil with sorbed TNT, an experiment was conducted

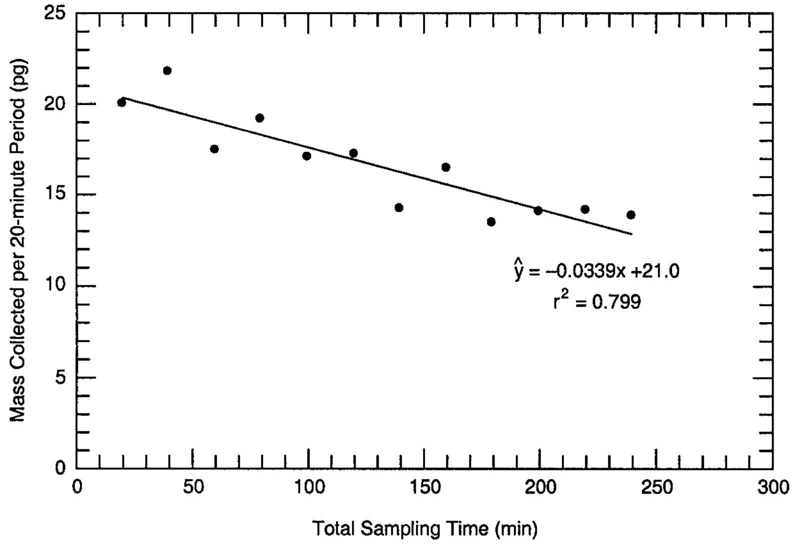

Figure 8. Continuous sampling of headspace vapor above moist Raritan Arsenal soil for TNT by alternating two polyacrylate SPME fibers at 20-minute intervals at 23°C.

with a soil from Raritan Arsenal that was field contaminated with a low concentration of TNT (about 1.4 mg/kg). A 3.02-g portion of the soil was moistened with water (5% water, on a dry weight basis) and allowed to equilibrate for 3 days in a 40-mL amber vial. The headspace in the vial was then sampled continuously for 200 minutes using two polyacrylate fibers as described above. The results are shown in Figure 8. Using the best fit linear equation, we find that the mass collected in the first 20 minutes was 20.4 pg, while the mass recovered in the second 20-minute sampling period was 19.8 pg. The reduction from the first to the second sampling periods amounts to only about 3% and, hence, the assumption that the vapor concentration is constant over the sampling period when the TNT is sorbed on soil particles is valid.

These results demonstrate that the approach of sampling the headspace using SPME fibers does not substantially reduce the vapor concentration of TNT during a 20-minute exposure period. Since the mass of TNT collected with time is linear, probably controlled by the diffusion rate of TNT away from the surface of the fiber, it may be possible to calibrate the volume of vapor sampled as a function of exposure time for a given chemical. One way this could be done is to sample a headspace volume where the concentration of TNT in the vapor was known, and from mass calibration of the TNT collected, the volume sampled as a function of time can be calculated from

$$\text{volume sampled (mL)} = \text{mass collected (g)}$$

$$\div \text{ vapor concentration (g/mL)}. \qquad (1)$$

Because the vapor pressure of TNT is low and TNT is known to be very sorptive to surfaces, trying to establish a known vapor concentration by injection of a given mass of TNT into a known volume of air is impractical. On the other hand, the vapor pressure of TNT as a function of temperature has been measured by a number of investigators (Pella 1977, Leggett et al. 1977, etc.). Results from the various investigators vary somewhat, but we believe the values published by Pella (1977) are the most reliable. Pella used a liquid solvent to trap the equilibrium vapor from a known volume of gas, minimizing sorption effects, and reducing the problem to a chromatographic analysis against standard solutions in the same matrix. This type of experiment should be accurate and precise to a few percent.

The vapor pressure of TNT (p) at 23°C according to Pella is 6.71×10^{-6} torr ([log10 (p in torr) = $(12.31 \pm 0.34) - (5175 \pm 105)\ T$, where T is the absolute temperature in kelvins]). This converts to a vapor concentration of 8.25×10^{-8} g/L. When we exposed a polyacrylate SPME fiber to the equilibrium vapor above military-grade TNT (Picatinny Arsenal, 1966 vintage) and determined the mass of TNT sorbed by the fiber using GC-µECD in a 20-minute exposure period, we collected 3.8×10^{-9} g of TNT. Computing the volume sampled from

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eq 1, we obtained a sampling volume of 46 mL for a 20-minute exposure period. Since the amount sampled is linearly related to exposure period, the effective sampling rate for TNT with the polyacrylate fiber is about 2.3 mL/minute at 23°C.

Since the three major vapor signature chemicals from military-grade TNT are 2,4-DNT and 2,6-DNT (Murrmann et al. 1971, Leggett et al. 1977), and 1,3-DNB (discussed above), it is also important to be able to calculate the vapor concentrations for these substances. In order to do so, we need to know the effective sampling rate for these compounds using the polyacrylate fiber. The vapor pressures of 2,4-DNT, 2,6-DNT, and 1,3-DNB are 1.44×10^{-4}, 3.71×10^{-4} (Pella 1977), and 6.22×10^{-4} torr (Howard and Maylan 1997, extrapolated) at 22°C, respectively, and the resulting vapor concentrations are 1.42×10^{-9}, 3.67×10^{-9}, and 5.68×10^{-9} g/mL, respectively. These concentrations result in masses collected on the fiber that are above the linear range of the μECD when SPME exposure periods are more than a few minutes. The nitrogen-phosphorus detector (NPD) is selective for nitrogen-containing compounds, but is not nearly as sensitive as the μECD. Thus, to calibrate the effective sampling rates for 2,4-DNT, 2,6-DNT, and 1,3-DNB, 50-mg portions of SARM-grade material for each compound were placed in individual 40-mL amber vials and the headspace equilibrated for 7 days. The headspace above each compound was sampled by exposing polyacrylate SPME fibers to the respective headspace in the vial for periods ranging between 1 and 30 minutes and desorbing the fibers in the injector of a GC-NPD (SRI Instruments Model 8610). The mass of each compound was determined against SARM-based standards prepared in acetone.

A plot of the mass of 2,4-DNT recovered from the fiber as a function of sorption time is presented in Figure 9. Inspection of the data indicates that a linear model with zero intercept adequately describes them over the entire sorption period tested. The slope of the linear model between mass sorbed (ng) and sorption time is 6.30, with a correlation coefficient of 0.989. When we solved this equation for the mass sorbed at 20 minutes, we obtained 126 ng. Using this value in eq 1, along with the equilibrium vapor concentration calculated from the vapor pressure (1.424×10^{-9} g/mL), we calculated a sampling volume of about 88.5 mL for a 20-minute sampling time, or an effective sampling rate of 4.45 mL/min at 23°C. This sampling volume is about double that obtained for 2,4,6-TNT at 23°C.

Similarly, plots of the masses of 2,6-DNT and 1,3-DNB recovered as a function of sorption time are presented in Figures 10 and 11. In both cases, the mass recovered as a function of sampling time was adequately described by linear models with correlation coefficients of 0.992. When an effective sampling volume for 2,6-DNT was computed, as described for 2,4-DNT, a sampling volume of 81.1 mL was obtained for a 20-minute sorption period, which is 4.05 mL/min at 23°C. This value compares favorably with 4.45 mL/min for 2,4-DNT at the same temperature. Since these two species are geometric isomers of one another, with the two

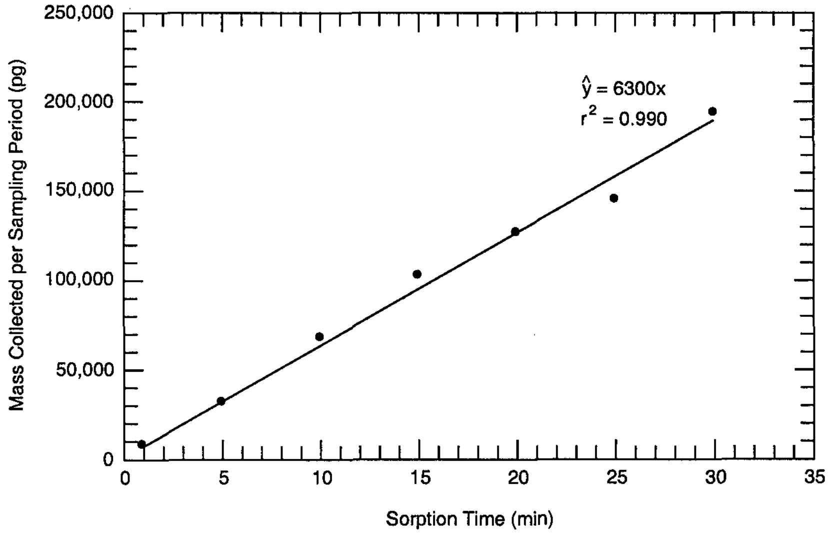

Figure 9. Mass of 2,4-DNT vapor sorbed on a polyacrylate SPME fiber at 23°C.

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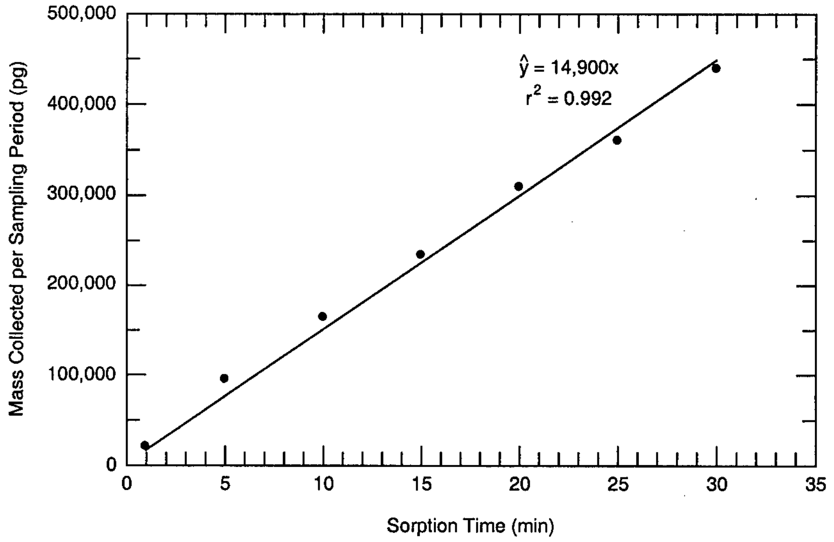

Figure 10. Mass of 2,6-DNT vapor sorbed on a polyacrylate SPME fiber at 23°C.

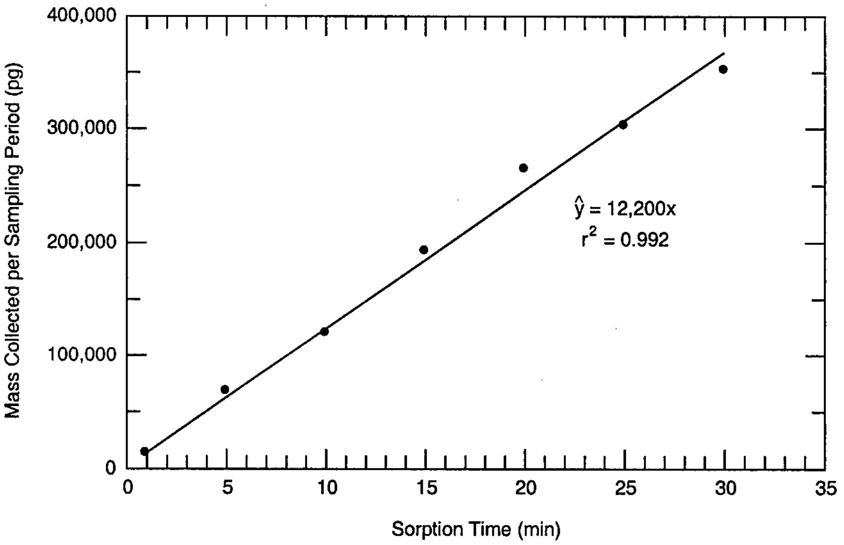

Figure 11. Mass of 1,3-DNB vapor sorbed on a polyacrylate SPME fiber at 23°C.

nitro groups oriented meta to each other, it is not unexpected that sampling volumes, probably controlled by the rate of diffusion in the polyacrylate fiber, would be quite similar. In addition, the vapor pressure estimates used to estimate these volumes were obtained from the same source (Pella 1977).

When we obtained an estimate of the effective sampling volume for 1,3-DNB from the data shown in Figure 11, however, we estimated a sampling volume of 43.1 mL for the 20-minute sorption period, or an effective sampling volume of 2.16 mL/min at 23°C. This volume is similar to the 2.3-mL/min sampling volume we obtained for 2,4,6-TNT, but is only about one-half of that obtained for the two isomers of DNT. The estimate of vapor pressure for this compound was obtained by extrapolation of data at higher temperatures and we do not feel that this value is as reliable as the vapor pressure data for 2,4- and 2,6-DNT.

Effective sampling rates were obtained for 2,4,6-TNT, 2,4-DNT, and 2,6-DNT in a similar manner at 4 and −12°C, using SARM-grade material. Effective sampling rates for these compounds as a function of temperature are presented in Table 7.

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Table 7. Effective sampling rates (mL/min) for 2,4,6-TNT, 2,4-DNT, 2,6-DNT, and 1,3-DNB as a function of temperature.

Compound	*23°C*	*4°C*	*–12°C*
2,4,6-TNT	2.30	4.70	3.71
2,4-DNT	4.45*	5.50	10.3
2,6-DNT	4.05*	5.10	13.7
1,3-DNB	2.16*	†	†

* Value obtained at 22°C.
† No estimate for vapor pressure available.

Vapor concentrations of signature chemicals in soil headspace samples

Peak heights for the target analytes detected in the soil headspace SPME samples were converted to mass (ng) using SARM-based standards prepared in acetonitrile. Peak heights for 2,5-DNT and 3-5-DNT were converted to mass of analyte recovered using the response factors for 2,4-DNT. After locating a source for these analytes, we made the standards and compared the detector response to the response for the 2,4-DNT standard. A response conversion factor was applied to 2,5-DNT and 3,5-DNT so that these analytes could be expressed as their own concentrations. Individual values for the vapor concentration of each target analyte in the two replicates for each combination of soil type, moisture level, and temperature for each day when samples were collected are presented in Appendix A, Tables A1–A9.

The mass of each target analyte detected in each headspace sample was converted to vapor concentration (pg/mL) using the effective sampling rates (mL/min), which were obtained as described in the *Calibration of SPME* section, and the sampling times (minutes) for each temperature. The effective sampling rate for 2,4,6-TNT (2.3 mL/min) was used to compute vapor concentrations for 2,4,6-TNT and other compounds containing three nitro functions. The effective sampling rate obtained for 2,4-DNT (4.5 mL/min) was used to estimate vapor concentrations of 2,4-DNT. Vapor concentrations for the other dinitro-containing compounds (DNTs and DNBs) were estimated from the mean effective sampling rates measured for 2,4-DNT and 2,6-DNT (4.3 mL/min). The effective sampling rate estimate for 1,3-DNB was not used because we judged the vapor pressure data that served as the basis for this value to be unreliable. These concentrations for each headspace sample analyzed are presented in Tables A10–A18.

Mean vapor concentrations for the two replicates for each of the three moisture conditions for Ottawa sand at 23, 4, and –12°C are presented in Table 8. Similarly, mean concentrations for headspace vapors for the silty and clayey soils at the three temperatures are presented in Tables 9 and 10, respectively. Because of the numbers of individual treatment conditions in this experiment, we were unable to analyze individual replicates with the frequency needed to accurately establish the breakthrough times for the various vapors to penetrate the soil barrier and be detectable in the headspace. Nevertheless, we did detect the presence of 2,4-DNT and 2,4,6-TNT in the headspace above the sand and silt soils maintained at 23°C at day 6 for all three moisture levels, and at day 15 above the clay for the two higher moisture levels. At 4°C, 2,4-DNT and 2,4,6-TNT were detected in the vapor above the sand and silt for all three moisture levels at 12 days. For the clay, 2,4-DNT was detected at 19 days above the 4°C samples, but 2,4,6-TNT was not detected until day 67, and then only at the two higher moisture levels. For the –12°C samples, 2,4-DNT was detectable in the headspace at day 13 above the sand and silt soils, but 2,4,6-TNT was not detected until day 173. For the clay at –12°C, only at day 173 was either 2,4-DNT or 2,4,6-TNT detectable.

Figure 12 is a plot of the vapor concentrations of 2,4-DNT, 1,3-DNB, and 2,4,6-TNT in the headspace above the silty soil at 23°C (low moisture added), as a function of time after the start of the experiment (4–112 days); 2,4-DNT and 1,3-DNB have the highest concentration of the target analytes throughout the study. For example, at 112 days, 2,4-DNT was present in the headspace at 28.9 ng/L, and 1,3-DNB was present at 15.5 ng/L. In comparison, the vapor concentration of 2,4,6-TNT was only 2.65 ng/L after 112 days (Table 9).

In the headspace above the Ottawa sand held at 23°C, vapor concentrations of the target analytes exceeded those found above the silty soil by about an order of magnitude (Table 8). For example, the concentrations of 2,4-DNT, 1,3-DNB, and 2,4,6-TNT at 112 days in the low-moisture case were 604, 401, and 135 ng/L, respectively. Conversely, for the clayey soil (low moisture, 23°C), headspace concentrations were about an order of magnitude lower than for the silt. At 112 days, the vapor concentrations of 2,4-DNT, 1,3-DNB, and 2,4,6-TNT were 8.98, 1.68, and 0.24 ng/L, respectively (Table 10). These three analytes were generally the target analytes present at highest concentration in the headspace vapor above all three soils maintained at 23°C, although occasionally

Table 8. Mean analyte concentrations (pg/mL) in headspace vapor above sand containing buried U.S. military-grade TNT, at three temperatures and three moisture levels.

	23°C			*4°C*			*−12°C*		
Analyte	*Air dry*	*2.10%*	*3.10%*	*Air dry*	*2.10%*	*3.10%*	*Air dry*	*2.10%*	*3.10%*
		6 days							
1,3-DNB	8.21	116	66.7						
1,2-DNB	4.37	21.5	13.7						
2,5-DNT	*<0.544*	*<14.3*	8.59						
2,4-DNT	0.700	151	105						
3,5-DNT	<d	*<40.7*	26.5						
1,3,5-TNB	<d	<d	<d						
2,4,6-TNT	0.125	7.76	10.1						
		15 days			**12 days**			**13 days**	
1,3-DNB	115	171	87.7	<d	7.05	6.39	<d	<d	<d
1,2-DNB	30.6	34.0	18.8	0.023	1.48	1.42	<d	<d	<d
2,5-DNT	8.74	15.8	7.96	<d	1.05	1.00	<d	<d	<d
2,4-DNT	16.5	**>203**	172	0.132	7.12	6.82	0.015	0.103	0.059
3,5-DNT	4.35	55.6	34.3	<d	2.23	2.00	<d	<d	<d
1,3,5-TNB	<d	1.84	1.17	<d	<d	<d	<d	<d	<d
2,4,6-TNT	3.42	23.8	19.2	0.371	0.980	1.91	<d	<d	<d
		22 days			**19 days**			**20 days**	
1,3-DNB	15.0	*267*	107	*<0.036*	33.6	12.4	<d	<d	<d
1,2-DNB	7.52	*43.1*	22.4	*<0.008*	6.50	2.90	<d	<d	<d
2,5-DNT	0.464	*15.0*	8.09	*<0.017*	3.64	1.39	<d	<d	<d
2,4-DNT	6.23	***>306***	208	0.102	44.9	21.3	0.042	0.032	0.034
3,5-DNT	0.699	*77.6*	*27.2*	0.031	9.33	4.74	<d	<d	<d
1,3,5-TNB	<d	*17.20*	2.39	*<0.063*	*<0.082*	0.071	<d	<d	<d
2,4,6-TNT	0.476	*30.8*	40.4	0.950	1.58	2.56	<d	<d	<d
		34 days			**35 days**			**36 days**	
1,3-DNB	64.8	207	146	<d	45.5	30.3	<d	1.00	0.592
1,2-DNB	22.3	39.7	29.9	<d	9.61	6.59	<d	0.101	0.058
2,5-DNT	4.97	14.6	10.7	<d	5.15	3.31	<d	0.046	0.027
2,4-DNT	43.6	**>298**	**>260**	0.030	69.6	50.2	0.045	0.042	0.044
3,5-DNT	*<6.06*	78.2	60.2	<d	14.7	*<10.7*	<d	<d	<d
1,3,5-TNB	<d	16.5	8.72	<d	0.243	0.249	<d	<d	<d
2,4,6-TNT	6.90	147	147	0.033	4.22	6.36	<d	<d	<d
		63 days			**67 days**			**69 days**	
1,3-DNB	66.5	348	212	<d	40.6	32.2	<d	4.19	3.30
1,2-DNB	22.1	64.0	40.0	<d	9.20	7.00	<d	0.420	0.316
2,5-DNT	4.75	26.2	14.5	<d	5.22	3.93	<d	0.197	0.144
2,4-DNT	34.9	**>168**	**>211**	0.030	66.1	52.6	0.026	0.501	0.316
3,5-DNT	4.56	227	70.7	<d	13.0	10.4	<d	0.065	*<0.054*
1,3,5-TNB	<d	11.5	6.51	<d	0.103	0.113	<d	*<0.021*	*<0.019*
2,4,6-TNT	3.19	101	96.8	0.010	2.73	3.70	<d	0.014	0.011
		112 days			**111 days**			**110 days**	
1,3-DNB	*5.86*	*401*	*231*	<d	*47.8*	*31.8*	<d	*7.76*	*7.43*
1,2-DNB	*3.58*	*76.3*	*44.9*	<d	*10.6*	*7.19*	*0.032*	*0.830*	*0.760*
2,5-DNT	*0.407*	*25.2*	*16.6*	<d	*6.36*	*4.15*	<d	*0.403*	*0.365*
2,4-DNT	*1.93*	*604*	*427*	*0.018*	*82.0*	*56.5*	*0.026*	*1.38*	*1.31*
3,5-DNT	*0.267*	*125*	*85.6*	<d	*16.7*	*11.4*	<d	*0.218*	*0.203*
1,3,5-TNB	<d	*8.59*	*2.96*	<d	<d	<d	<d	<d	<d
2,4,6-TNT	*0.542*	*135*	*97.7*	*0.006*	*2.28*	*1.61*	<d	<d	<d
					173 days			**173 days**	
1,3-DNB				<d	not done		<d	not done	
1,2-DNB				*0.080*				*0.074*	
2,5-DNT				<d				<d	
2,4-DNT				*0.020*				*0.010*	
3,5-DNT				<d				<d	
1,3,5-TNB				*0.010*				<d	
2,4,6-TNT				*0.042*				*0.016*	

<d	Values were less than the detection limit.
bold	One replicate had a value greater than the detector maximum signal.
bold	Only values available were greater than the detector maximum signal.
italics	One of the replicate values was less than the detection limit.
italics	Only one replicate was analyzed.

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Table 9. Mean analyte concentrations (pg/mL) in headspace vapor above silt containing buried U.S. military-grade TNT, at three temperatures and three moisture levels.

	23°C			*4°C*			*−12°C*		
Analyte	*Air dry*	*5.8%*	*10%*	*Air dry*	*5.8%*	*10%*	*Air dry*	*5.8%*	*10%*
		6 days							
1,3-DNB	<d	14.5	11.8						
1,2-DNB	<d	6.88	1.96						
2,5-DNT	<d	2.11	0.438						
2,4-DNT	0.047	20.1	11.4						
3,5-DNT	<d	5.00	3.53						
1,3,5-TNB	<d	<d	<d						
2,4,6-TNT	0.317	0.717	0.731						
		15 days			**12 days**			**13 days**	
1,3-DNB	<*0.200*	17.9	*18.5*	<d	1.35	1.53	<d	<d	<d
1,2-DNB	<*0.051*	2.06	*2.54*	<d	0.281	0.320	<d	<d	<d
2,5-DNT	<*0.021*	0.220	*0.297*	<d	0.081	0.103	<d	<d	<d
2,4-DNT	0.264	29.5	*33.4*	0.063	0.550	0.790	0.039	0.038	0.028
3,5-DNT	<*0.146*	4.74	*5.4*	<d	0.184	0.195	<d	<d	<d
1,3,5-TNB	<*0.073*	<*0.089*	<d	<d	<d	<d	<d	<d	<d
2,4,6-TNT	0.153	0.554	*0.854*	0.224	0.593	0.515	<d	<d	<d
		22 days			**19 days**			**20 days**	
1,3-DNB	<d	22.8	18.8	<d	*2.22*	3.22	<d	<d	<d
1,2-DNB	<d	2.30	2.70	<d	*0.463*	0.670	<d	<d	<d
2,5-DNT	<d	<*0.225*	0.265	<d	*0.112*	0.186	<d	<d	<d
2,4-DNT	0.039	38.3	37.8	0.036	*1.80*	2.95	0.039	0.044	0.029
3,5-DNT	<d	<*7.47*	6.53	<d	*0.390*	0.600	<d	<d	<d
1,3,5-TNB	<d	0.091	0.084	<d	<d	<d	<d	<d	<d
2,4,6-TNT	0.048	0.743	2.72	<*0.209*	*0.047*	0.180	<d	0.032	<d
		34 days			**35 days**			**36 days**	
1,3-DNB	<*0.039*	25.8	20.1	<d	9.59	6.97	<d	*0.038*	<d
1,2-DNB	0.039	2.56	2.92	<d	1.85	1.43	<d	<d	<d
2,5-DNT	<d	0.175	0.288	<d	0.390	0.416	<d	<d	<d
2,4-DNT	0.062	51.6	45.5	0.026	8.71	8.29	0.035	0.032	0.032
3,5-DNT	<d	<*9.28*	8.15	<d	1.74	<*1.45*	<d	<d	<d
1,3,5-TNB	<d	0.158	0.095	<d	<d	<d	<d	<d	<d
2,4,6-TNT	0.133	2.13	6.99	<d	0.282	0.206	<d	*0.048*	<d
		63 days			**67 days**			**69 days**	
1,3-DNB	<*0.040*	28.0	23.3	<d	12.5	9.53	<d	<d	<d
1,2-DNB	0.051	2.64	3.31	0.007	2.22	1.72	<d	<d	<d
2,5-DNT	<*0.010*	0.160	0.354	<d	0.458	0.410	<d	<d	<d
2,4-DNT	0.057	53.2	46.5	0.036	12.0	10.7	0.027	0.021	0.034
3,5-DNT	<*0.041*	8.54	7.92	<*0.016*	2.30	2.06	<d	<d	<d
1,3,5-TNB	<d	0.083	0.740	<d	<d	<d	<d	<d	<d
2,4,6-TNT	0.365	2.55	8.63	<*0.019*	0.254	0.509	<d	<d	<d
		112 days			**111 days**			**110 days**	
1,3-DNB	<d	*15.5*	*14.2*	<d	*9.29*	*7.53*	<d	<d	<d
1,2-DNB	*0.029*	*1.67*	*2.17*	<d	*1.49*	*1.31*	<d	*0.016*	<d
2,5-DNT	<d	*0.113*	*0.245*	<d	*0.287*	*0.364*	<d	<d	<d
2,4-DNT	*0.028*	*28.9*	*29.1*	*0.037*	*9.38*	*9.72*	*0.024*	*0.026*	*0.013*
3,5-DNT	<d	*5.28*	*5.42*	<d	*1.83*	*<d*	<d	<d	<d
1,3,5-TNB	<d	*0.388*	*1.37*	<d	*<d*	*<d*	<d	<d	<d
2,4,6-TNT	<d	*2.65*	*8.77*	<d	*0.179*	*0.329*	<d	<d	<d
		173 days			**173 days**			**173 days**	
1,3-DNB	*0.013*	not done		<d	not done		<d	*0.168*	<d
1,2-DNB	*0.010*				<d		<d	*0.081*	*0.009*
2,5-DNT	<d				<d		<d	<d	<d
2,4-DNT	*0.015*				*0.012*		*0.037*	*0.018*	*0.010*
3,5-DNT	<d				<d		<d	<d	<d
1,3,5-TNB	*0.021*				<d		<d	<d	*0.012*
2,4,6-TNT	*0.017*				*0.011*		*0.163*	*0.016*	*0.006*

<d	Values were less than the detection limit.
bold	One replicate had a value greater than the detector maximum signal.
bold	Only values available were greater than the detector maximum signal.
italics	One of the replicate values was less than the detection limit.
italics	Only one replicate was analyzed.

Table 10. Mean analyte concentrations (pg/mL) in headspace vapor above clay containing buried U.S. military-grade TNT, at three temperatures and three moisture levels.

	23°C			*4°C*			*−12°C*		
Analyte	*Air dry*	*5.8%*	*10%*	*Air dry*	*5.8%*	*10%*	*Air dry*	*5.8%*	*10%*
	6 days								
1,3-DNB	<d	0.533	0.457						
1,2-DNB	<d	0.290	0.259						
2,5-DNT	<d	*<0.013*	<d						
2,4-DNT	<d	<d	<d						
3,5-DNT	<d	5.24	4.14						
1,3,5-TNB	<d	<d	<d						
2,4,6-TNT	<d	<d	<d						
	15 days			**12 days**			**13 days**		
1,3-DNB	<d	*1.70*	*1.19*	<d	<d	<d	<d	<d	<d
1,2-DNB	<d	*0.326*	*0.221*	<d	<d	<d	<d	<d	<d
2,5-DNT	<d	*0.090*	*0.030*	<d	<d	<d	<d	<d	<d
2,4-DNT	<d	*1.72*	*0.994*	<d	0.800	*0.840*	<d	<d	<d
3,5-DNT	<d	*0.867*	*0.217*	<d	<d	<d	<d	<d	<d
1,3,5-TNB	<d	*0.222*	*0.090*	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	*0.442*	*0.351*	<d	<d	<d	<d	<d	<d
	22 days			**19 days**			**20 days**		
1,3-DNB	<d	1.74	1.60	<d	*<0.075*	0.080	<d	<d	<d
1,2-DNB	<d	0.279	0.258	<d	0.041	0.036	<d	<d	<d
2,5-DNT	<d	*<0.077*	0.061	<d	<d	<d	<d	<d	<d
2,4-DNT	<d	3.54	2.75	0.028	0.042	0.063	<d	<d	<d
3,5-DNT	<d	*<0.711*	0.479	<d	<d	<d	<d	<d	<d
1,3,5-TNB	<d	0.177	0.175	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	0.297	0.294	<d	<d	<d	<d	<d	<d
	34 days			**35 days**			**36 days**		
1,3-DNB	<d	2.33	1.92	<d	0.502	0.64	<d	<d	<d
1,2-DNB	<d	0.332	0.274	<d	0.155	0.160	<d	<d	<d
2,5-DNT	<d	0.042	0.049	<d	<d	<d	<d	<d	<d
2,4-DNT	<d	8.04	6.03	0.031	0.069	0.351	<d	<d	<d
3,5-DNT	<d	0.882	0.653	<d	0.052	0.083	<d	<d	<d
1,3,5-TNB	<d	0.169	0.283	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	0.207	0.163	<d	<d	<d	<d	<d	<d
	63 days			**67 days**			**69 days**		
1,3-DNB	<d	1.37	1.13	<d	1.12	0.451	<d	<d	<d
1,2-DNB	<d	0.254	0.228	<d	0.178	0.127	<d	<d	<d
2,5-DNT	<d	0.015	0.014	<d	*<0.007*	*<0.012*	<d	<d	<d
2,4-DNT	<d	6.05	4.86	0.034	0.432	1.22	<d	<d	<d
3,5-DNT	<d	0.681	0.551	<d	0.125	0.171	<d	<d	<d
1,3,5-TNB	<d	0.195	0.193	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	0.129	0.103	<d	*<0.012*	0.016	<d	<d	<d
	112 days			**111 days**			**110 days**		
1,3-DNB	<d	*1.68*	*1.44*	<d	*1.34*	*0.100*	<d	<d	<d
1,2-DNB	<d	*0.398*	*0.355*	<d	*0.169*	*0.070*	<d	<d	<d
2,5-DNT	<d	*0.013*	*0.013*	<d	*0.009*	*0.008*	<d	<d	<d
2,4-DNT	<d	*8.98*	*7.46*	<d	*1.00*	*1.13*	<d	<d	<d
3,5-DNT	<d	*1.19*	*0.994*	<d	*0.140*	*0.131*	<d	<d	<d
1,3,5-TNB	<d	*0.311*	*0.309*	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	*0.239*	*0.231*	<d	*0.025*	*0.030*	<d	<d	<d
	173 days			**173 days**			**173 days**		
1,3-DNB	<d	not done		<d	not done		<d	<d	*0.017*
1,2-DNB	<d			<d			<d	<d	*0.005*
2,5-DNT	<d			<d			<d	<d	<d
2,4-DNT	*0.010*			*0.010*			*0.010*	*0.026*	*0.021*
3,5-DNT	<d			<d			<d	<d	<d
1,3,5-TNB	<d			<d			<d	*0.011*	*0.016*
2,4,6-TNT	*0.007*			*0.007*			*0.005*	*0.107*	*0.047*

<d	Values were less than the detection limit.
bold	One replicate had a value greater than the detector maximum signal.
bold	Only values available were greater than the detector maximum signal.
italics	One of the replicate values was less than the detection limit.
italics	Only one replicate was analyzed.

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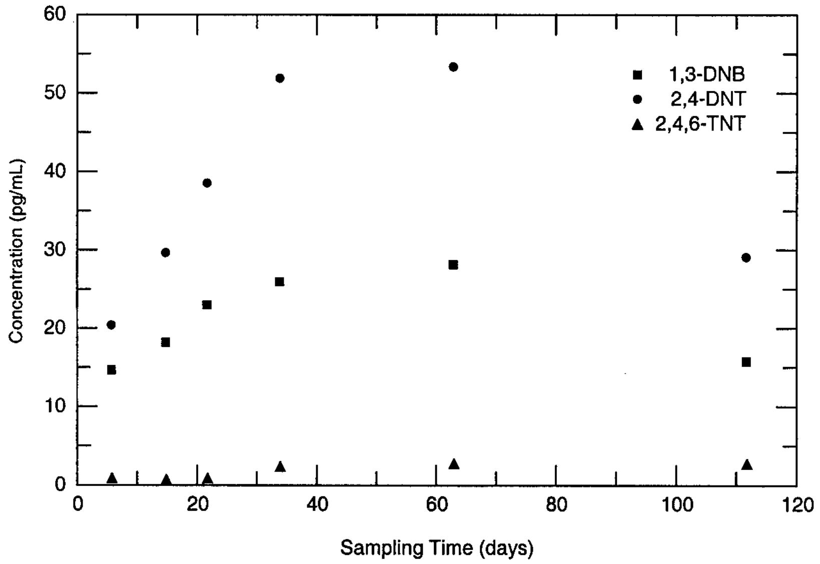

Figure 12. Concentration of analytes in the headspace vapor above 5.8% moist silt containing buried TNT at 23°C.

the concentration of either 1,2-DNB or 1,3,5-TNB exceeded that for 2,4,6-TNT.

The vapor concentrations of target analytes in the headspace above the air-dried soils were much lower than those above the moist soils. In fact, only at 23°C above the Ottawa sand (Table 8) were target analytes routinely measurable in the vapor (concentrations exceeding 0.01 ng/L). After 63 days, for example, the vapor concentrations of 2,4-DNT, 1,3-DNB, and 2,4,6-TNT were 34.9, 66.5, and 3.19 ng/L, respectively. For moist soils, the vapor concentrations of 2,4-DNT generally exceeded those of 1,3-DNB, but for air-dried soils, vapor concentrations of 1,3-DNB generally exceeded 2,4-DNT.

At lower temperatures (4 and −12°C), vapor concentrations were much lower than at 23°C, reflecting the exponential dependence of vapor pressure on temperature. For example, the vapor concentrations of 2,4-DNT, 1,3-DNB, and 2,4,6-TNT above the Ottawa sand at 4°C were only 82.0, 47.8, and 2.28 ng/L for the low-moisture-added case at 111 days. This was about an order of magnitude reduction from that found for the corresponding sample held at 23°C for 2,4-DNT and 1,3-DNB, and an even greater reduction for the less volatile 2,4,6-TNT. For the silty soil, a similar reduction from 23°C was also observed for the 4°C samples. For example, vapor concentrations of 2,4-DNT, 1,3-DNB, and 2,4,6-TNT were 9.38, 9.29, and 0.18 ng/L, respectively, for the silty soil with low moisture added at 111 days. The magnitude of reduction from the corresponding sample at 23°C was again greatest for 2,4,6-TNT.

For the clayey soil maintained at 4°C, the vapor concentrations were reduced to less than detection limits for all analytes except 2,4-DNT, 1,3-DNB, 1,2-DNB, and 2,4,6-TNT. Even after 111 days, vapor concentrations of 2,4-DNT and 1,3-DNB were only 1.00 and 1.34 ng/L, respectively, for the low-moisture-added case, and the concentration of 2,4,6-TNT was less than 0.03 ng/L.

At −12°C, vapor concentrations were further reduced; only for the moist Ottawa sand did vapor concentrations exceed detection limits (0.01 ng/L). At 110 days for the low-moisture sand sample, vapor concentrations of 2,4-DNT, 1,3-DNB, and 1,2-DNB were 1.38, 7.76, and 0.83 ng/L, respectively, and the concentration of 2,4,6-TNT was below detection limits. While all concentrations were greatly reduced from 4°C, the reductions were greater for 2,4-DNT and 2,4,6-TNT, compared with the more volatile 1,3- and 1,2-DNB.

Accumulation of explosives residues on surface soils

After the time course of the vapor sampling was completed, the vials were opened and the top 5 mm of surface soil was carefully removed and analyzed to determine the concentrations of target analytes that had migrated to the surface. There were two replicates for each combination of soil type, moisture status, and temperature. One replicate for each combination was sampled on day 63, just after the vapor was sampled with a SPME fiber. Surface soil from the second repli-

Table 11. Analyte concentration (mg/kg) in the surface of test soils after 63, 112, or 173 days.

Moisture status	*1,3,5-TNB*	*1,3-DNB*	*2,4,6-TNT*	*1,2-DNB*	*2,4-DNT*	*2ADNT*	*4ADNT*
			a. Ottawa sand				
63 days							
			23°C				
Air-dried		0.877	1.23	0.182	1.52		
Low moisture	0.579	0.745	1.32	0.190	1.11		
High moisture	0.455	0.618	1.82	0.136	0.992		
			4°C				
Air-dried			0.156				
Low moisture	0.227	0.775	0.534	0.182	1.14		
High moisture	0.202	0.538	0.838	0.129	0.769		
			–12°C				
Air-dried			0.767				
Low moisture		0.059			0.045		
High moisture		0.027					
112 days or 173 days*							
			23°C				
Air-dried*		0.926	1.07	0.186	1.48	0.142	
Low moisture	0.614	0.591	1.70	0.134	0.894		
High moisture	0.512	0.535	2.28	0.126	0.880	0.550	
			4°C				
Air-dried*				0.075			
Low moisture	0.225	0.575	0.679	0.150	0.911		
High moisture	0.235	0.575	0.871	0.143	0.896	0.254	
			–12°C				
Air-dried*		0.067					
Low moisture		0.206			0.129		
High moisture		0.172	0.042		0.127		
			b. Hitchcock silt				
63 days							
			23°C				
Air-dried							
Low moisture	0.153	0.546	0.421		1.60		
High moisture	0.956	0.588	1.85		1.50		
			4°C				
Air-dried			0.148				
Low moisture		0.946	0.137	0.215	1.67		
High moisture	0.023	0.751	0.499	0.152	1.23		
			–12°C				
Air-dried			0.161				
Low moisture							
High moisture							
112 days or 173 days*							
			23°C				
Air-dried*	0.656	0.179	0.112	0.195	0.045		
Low moisture	1.25	0.435	0.981		1.28		
High moisture	2.77	0.53	3.10		1.35	0.441	
			4°C				
Air-dried*			0.099				
Low moisture		0.802	0.181	0.147	1.37		
High moisture	0.100	0.925	0.898	0.191	1.66		
			–12°C				
Air-dried*		0.017	0.062				
Low moisture*		0.200	0.023	0.070	0.119		
High moisture*		0.086	0.030	0.057	0.051		

* Values measured at 173 days; others measured at 112 days.

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Table 11 (cont'd). Analyte concentration (mg/kg) in the surface of test soils after 63, 112, or 173 days.

Moisture status	*1,3,5-TNB*	*1,3-DNB*	*2,4,6-TNT*	*1,2-DNB*	*2,4-DNT*	*2ADNT*	*4ADNT*
			c. Ft. Edwards clay				
63 days							
			23°C				
Air-dried							
Low moisture		0.228	0.239		1.51		
High moisture		0.242	0.335		1.57		
			4°C				
Air-dried							
Low moisture		0.736			0.631		
High moisture		0.343	0.759		1.46	0.173	0.463
			–12°C				
Air-dried			0.161				
Low moisture							
High moisture							
112 days							
			23°C				
Air-dried*			0.020				
Low moisture	0.156	0.198	0.874		1.44	0.603	0.692
High moisture	0.176	0.205	1.18		1.49	0.675	0.688
			4°C				
Air-dried*							
Low moisture	0.065	0.761	0.215		1.05		
High moisture	0.132	0.099	1.46		1.28		
			–12°C				
Air-dried*							
Low moisture*							
High moisture*							

* Values measured at 173 days; others measured at 112 days.

cate was sampled in a similar manner on day 112 for most combinations, again just after the vapor sample was collected. For several of the air-dried soil combinations, and some of the other combinations at –12°C, vapor analysis at 112 days indicated that target analytes were still below detection limits; thus, in these cases, soil samples for the second replicate were delayed until day 173 to give additional time for target analytes to make their way to the surface.

Results of the surface soil analysis for Ottawa sand are presented in Table 11a. Measurable concentrations of 2,4,6-TNT, 2,4-DNT, 1,3- and 1,2-DNB, and 1,3,5-TNB were obtained for samples held at 23 and 4°C. For samples held at –12°C, only 2,4-DNT, 1,3-DNB, and 2,4,6-TNT were detected. Concentrations of the various TNT-related analytes ranged from below a detection limit of about 0.02 mg/kg to 2.28 mg/kg for 2,4,6-TNT in a high-moisture sample held at 23°C for 112 days. Generally, the analytes in the soil with the highest concentrations were either 2,4,6-TNT or 2,4-DNT for samples held at 23 or 4°C, but it was 1,3-DNB for samples held at –12°C, confirming the higher mobility of this more volatile component at low temperatures. The similarity in concentrations measured for 2,4,6-TNT, 2,4-DNT, and 1,3-DNB demonstrate that crystalline TNT was not present in these samples, but rather that these analytes had migrated through the soil to the top few millimeters of surface soil.

In general, concentrations of TNT-related analytes were higher in soil samples held at 23°C than in those held at 4°C, and much higher than concentrations in samples held at –12°C. The concentrations of these analytes were often greater in the soils with added moisture, relative to their air-dried counterparts, but this was not always true for the Ottawa sand.

Concentrations of TNT-related analytes in the surface 5 mm in the silt soil ranged from less than detection (about 0.02 mg/kg) to 3.1 mg/kg for 2,4,6-TNT in the high-moisture soil held at 23°C for 112 days (Table 11b). More of these analytes was always accumulated in the moist soils than in the air-dried soils, and the greatest amounts were in the soils held at 23°C. Concentrations for soil samples held at –12°C were very low, always at or below 0.2 mg/kg. The analytes present at the highest concentrations were either 2,4,6-TNT or 2,4-DNT in soil samples held at 23°C, 2,4-DNT and 1,3-DNB in those held at 4°C, and 1,3-DNB in those held at –12°C. 1,3,5-TNB accumulated substantially, as well, in soil samples held at 23°C, with concentrations ranging from 0.153 to 2.77 mg/kg, depending on the moisture content and days held.

The accumulation of TNT-related analytes in the surface 5 mm of Ft. Edwards Clay was generally lower than in the sand and silt (Table 11c). TNT-related analytes were nearly always below detection for air-dried soils, regardless of the temperature. For the moistened soils, concentrations ranged from less than detection to 1.57 mg/kg for 2,4-DNT in the high-moisture soil at 63 days. The concentration of 2,4-DNT was higher than that for 2,4,6-TNT in nearly every case. Concentrations of 1,3-DNB were always less than 1.0 mg/kg in the surface of the clay soil.

Even though the two common environmental transformation products of TNT (2ADNT and 4ADNT) were occasionally detected in these soils, the accumulation of these analytes over this several-month experiment was much less than predicted from holding time studies (Grant et al. 1993, Maskarinec et al. 1991). This may indicate that analytes moving through the soil in the vapor state become more tightly associated with soil surfaces than what is normally encountered at higher concentrations at explosives-contaminated sites. At higher concentrations, these compounds may be present in soil solution to a greater extent.

Soil–air partition coefficients

Since soil concentrations of TNT-related analytes were obtained immediately after equilibrium headspace measurements were completed, it is possible to compute soil–air partition coefficients for each analyte from data obtained in this experiment. These partition coefficients are important because they compare the amount of target analyte present in the soil vs. what is present in air at equilibrium. This information can be important in deciding whether to concentrate sample acquisition efforts in the air or in the soil to detect mines.

Table 12 shows the effect of soil type, moisture, and temperature on soil–air partitioning of explosive vapors. Soil–air partition coefficients decrease with temperature, in keeping with the energetics of the sorption process. They are highest for clay and lowest for sand, and they are higher for airdry than moist soil, as suggested by the earlier discussion of headspace concentrations. From a detection standpoint, it is worth emphasizing that 1 mL of headspace vapor contains only one thousandth to less than one millionth the mass of analyte present as does 1 g of the associated soil. This suggests that more effort might be made to exploit the soil's natural ability to preconcentrate these vapors, in lieu of, or in addition to, pursuing more sensitive explosive vapor detectors.

Table 12. Soil–air partition coefficients ($K_{s/a}$) for TNT-related compounds.

Analyte	*Soil type*	*Moist soil*	*Air-dried soil*
	a. At 23°C		
2,4,6-TNT	Sand	1.6×10^4	3.9×10^5
	Silt	2.0×10^5	
	Clay	2.5×10^6	
2,4-DNT	Sand	5.5×10^3	4.4×10^4
	Silt	3.1×10^4	
	Clay	2.8×10^5	
1,3-DNB	Sand	2.4×10^3	1.3×10^4
	Silt	2.2×10^4	
	Clay	1.9×10^5	
	b. At 4°C		
2,4,6-TNT	Sand	3.1×10^5	1.6×10^7
	Silt	3.8×10^5	9.0×10^6
	Clay	3.0×10^7	
2,4-DNT	Sand	1.5×10^4	
	Silt	1.3×10^5	
	Clay	1.6×10^6	
1,3-DNB	Sand	1.6×10^4	
	Silt	7.7×10^4	
	Clay	6.0×10^5	
	c. At –12°C		
2,4,6-TNT	Sand		
	Silt	2.5×10^6	3.8×10^5
	Clay		
2,4-DNT	Sand	9.5×10^4	
	Silt	6.1×10^6	
	Clay		
1,3-DNB	Sand	2.5×10^4	
	Silt	8.5×10^5	
	Clay		

SUMMARY

Experiments were conducted to investigate the qualitative and quantitative effects of soil barriers at various temperatures on the vapor signature from buried military-grade TNT. Military-grade TNT (110 mg) was buried beneath 2.5 cm of either a sand, silt, or clay soil in a small glass vial. The vials were held at temperatures ranging from –12 to 23°C for times ranging between 63 and 173 days before the soil was removed and analyzed for explosives signatures. We sampled the headspace vapors in the vials periodically using polyacrylate SPME fibers after periods ranging from 6 to 173 days and quantified the signatures using GC-ECD and a non-equilibrium calibration procedure.

Qualitatively, the isomers of DNB, DNT, and TNT account for all of the vapors detected in the headspace above these soils. In general, 2,4-DNT, 1,3-DNB, and 2,4,6-TNT were the target analytes present at the highest concentrations in the headspace vapor above all three soils maintained at 23°C. At 4°C, vapor concentrations were reduced by at least a factor of ten; the reduction was greatest for 2,4,6-TNT, the signature chemical with the lowest vapor pressure. At –12°C, vapor concentrations were further reduced; reductions were greater for 2,4-DNT and 2,4,6-TNT, compared with the more volatile 1,3-DNB.

Concentrations were generally greater above sands than above silty soils, and greater above silts than clay. Soil moisture level was also an important variable in controlling headspace vapor concentrations. For air-dried soils, vapor concentrations were lower than for either of the higher moisture contents for all three soils at all temperatures where vapors could be detected.

Measurable concentrations of 2,4,6-TNT, 2,4-DNT, and 1,3-DNB were obtained in the top 5 mm of sand and silt held at all three temperatures. Lower concentrations of these chemicals were detected in the clay at 23°C, but concentrations were generally below detection limits at lower temperatures.

Soil–air partition coefficients were computed for samples that had detectable signatures in both the headspace and the surface soil. These partition coefficients are higher for 2,4,6-TNT than for 2,4-DNT or 1,3-DNB, they decrease as temperature increases, they are highest for clay and lowest for sand, and they are higher for air-dry than moist soil. At equilibrium, 1 mL of headspace vapor contains only one thousandth to less than one millionth the mass of signature present as does 1 g of the associated soil. Thus, it may be possible to use the natural preconcentration of signature vapors that takes place on surface soil to increase their detectability.

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APPENDIX A: DATA

Table A1. Analyte mass collected (pg/min) in headspace vapor above sand containing buried U.S. military-grade TNT, at 23°C, and three moisture levels.

	Air dry		*2.1% moisture*		*3.1% moisture*	
Sample	*Rep A*	*Rep B*	*Rep A*	*Rep B*	*Rep A*	*Rep B*
6 days						
1,3-DNB	29.3	41.2	561	433	285	289
1,2-DNB	16.5	21.1	106	79.2	57.9	59.8
2,5-DNT	2.34	<d	61.6	<d	35.9	37.9
2,4-DNT	2.36	3.93	754	600	441	497
3,5-DNT	<d	<d	175	<d	108	119
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	0.267	0.305	20.8	14.9	13.7	32.8
15 days						
1,3-DNB	252	738	1183	285	234	519
1,2-DNB	81.3	181	228	63.7	57.7	104
2,5-DNT	20.1	55.0	115	20.8	19.0	49.2
2,4-DNT	118	31.0	**>1260**	562	520	1024
3,5-DNT	10.5	26.9	370	108	101	193
1,3,5-TNB	<d	<d	3.91	4.55	3.22	2.18
2,4,6-TNT	7.32	8.39	69.2	40.1	33.0	55.2
22 days						
1,3-DNB	52.7	76.0	not done	1148	271	648
1,2-DNB	27.0	37.7		185	64.8	128
2,5-DNT	3.68	0.312		64.4	18.9	50.6
2,4-DNT	23.2	32.8		**>1378**	601	1270
3,5-DNT	2.49	3.51		334	117	<d
1,3,5-TNB	<d	<d		39.7	6.20	4.80
2,4,6-TNT	1.17	1.02		70.8	68.0	118
34 days						
1,3-DNB	235	322	543	1237	935	319
1,2-DNB	82.6	109	126	215	183	73.6
2,5-DNT	19.0	23.7	48.5	77.0	68.2	23.6
2,4-DNT	189	203	1138	**>1546**	**>1546**	791
3,5-DNT	26.0	<d	244	428	359	159
1,3,5-TNB	<d	<d	55.7	20.4	15.0	25.0
2,4,6-TNT	17.7	14.0	352	322	283	392
63 days						
1,3-DNB	295	277	1800	1187	1003	820
1,2-DNB	98.6	91.5	334	216	196	148
2,5-DNT	21.2	19.6	151	74.1	69.8	55.0
2,4-DNT	161	152	**>950**	564	**>950**	**>951**
3,5-DNT	19.9	19.3	527	1425	329	279
1,3,5-TNB	<d	<d	31.9	20.9	18.0	11.9
2,4,6-TNT	7.25	7.41	206	257	247	199
112 days						
1,3-DNB	not done	25.2	not done	1725	not done	994
1,2-DNB		15.4		328		193
2,5-DNT		1.75		108		71.3
2,4-DNT		8.67		2719		1923
3,5-DNT		1.15		538		368
1,3,5-TNB		<d		19.8		6.80
2,4,6-TNT		1.25		310		225

<d Values were less than the detection limit
> bold Value > detector maximum signal

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Table A2. Analyte mass collected (pg/min) in headspace vapor above sand containing buried U.S. military-grade TNT, at 4°C, and three moisture levels.

	Air dry		*2.1% moisture*		*3.1% moisture*	
Sample	*Rep A*	*Rep B*	*Rep A*	*Rep B*	*Rep A*	*Rep B*
12 days						
1,3-DNB	<d	<d	13.7	46.8	28.3	26.7
1,2-DNB	0.134	0.061	3.12	9.65	6.12	6.10
2,5-DNT	<d	<d	1.98	7.03	4.24	4.38
2,4-DNT	0.827	0.358	16.3	47.9	31.8	29.6
3,5-DNT	<d	<d	4.70	14.4	8.83	8.36
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	0.986	0.719	2.00	2.51	7.10	1.70
19 days						
1,3-DNB	0.153	<d	174	115	26.6	80.5
1,2-DNB	0.032	<d	30.3	25.5	6.22	18.7
2,5-DNT	0.072	<d	18.7	12.6	2.64	9.34
2,4-DNT	0.762	0.152	222	183	47.7	143
3,5-DNT	0.130	0.133	42.4	37.8	10.6	30.1
1,3,5-TNB	0.144	<d	<d	0.188	0.163	0.161
2,4,6-TNT	4.30	0.079	2.57	4.68	7.35	4.38
35 days						
1,3-DNB	<d	<d	242	149	119	141
1,2-DNB	<d	<d	47.0	35.7	27.0	29.6
2,5-DNT	<d	<d	27.2	17.0	12.0	16.4
2,4-DNT	0.148	0.121	354	273	214	237
3,5-DNT	<d	<d	68.8	57.8	46.2	<d
1,3,5-TNB	<d	<d	0.226	0.893	0.689	0.454
2,4,6-TNT	0.101	0.050	6.41	13.0	17.7	11.5
67 days						
1,3-DNB	<d	<d	164	185	123	154
1,2-DNB	<d	<d	36.5	42.6	24.7	35.5
2,5-DNT	<d	<d	20.2	24.7	13.9	19.9
2,4-DNT	0.139	0.130	274	321	198	275
3,5-DNT	<d	<d	50.1	62.1	36.9	53.0
1,3,5-TNB	<d	<d	0.171	0.300	0.160	0.359
2,4,6-TNT	0.030	0.017	3.83	8.73	5.25	11.8
111 days						
1,3-DNB	not done	<d	not done	206	not done	137
1,2-DNB		<d		45.6		30.9
2,5-DNT		<d		27.3		17.8
2,4-DNT		0.080		369		254
3,5-DNT		<d		71.7		49.2
1,3,5-TNB		<d		<d		<d
2,4,6-TNT		0.014		10.5		7.42
173 days						
1,3-DNB	not done	<d	not done	not done	not done	not done
1,2-DNB		0.346				
2,5-DNT		<d				
2,4-DNT		0.088				
3,5-DNT		<d				
1,3,5-TNB		0.023				
2,4,6-TNT		0.096				

<d Values were less than the detection limit.

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Table A3. Analyte mass collected (pg/min) in headspace vapor above sand containing buried U.S. military-grade TNT, at –12°C, and three moisture levels.

	Air dry		*2.1% moisture*		*3.1% moisture*	
Sample	*Rep A*	*Rep B*	*Rep A*	*Rep B*	*Rep A*	*Rep B*
13 days						
1,3-DNB	<d	<d	<d	<d	<d	<d
1,2-DNB	<d	<d	<d	<d	<d	<d
2,5-DNT	<d	<d	<d	<d	<d	<d
2,4-DNT	0.072	0.063	0.487	0.440	0.306	0.219
3,5-DNT	<d	<d	<d	<d	<d	<d
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	<d	<d	<d	<d	<d
20 days						
1,3-DNB	<d	<d	<d	<d	<d	<d
1,2-DNB	<d	<d	<d	<d	<d	<d
2,5-DNT	<d	<d	<d	<d	<d	<d
2,4-DNT	0.245	0.127	0.193	0.089	0.212	0.095
3,5-DNT	<d	<d	<d	<d	<d	<d
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	<d	<d	<d	<d	<d
36 days						
1,3-DNB	<d	<d	4.36	4.22	1.53	3.56
1,2-DNB	<d	<d	0.446	0.420	0.158	0.339
2,5-DNT	<d	<d	0.197	0.192	0.075	0.159
2,4-DNT	0.206	0.199	0.169	0.209	0.199	0.199
3,5-DNT	<d	<d	<d	<d	<d	<d
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	<d	<d	<d	<d	<d
69 days						
1,3-DNB	<d	<d	16.9	19.1	12.1	16.3
1,2-DNB	<d	<d	1.74	1.87	1.17	1.54
2,5-DNT	<d	<d	0.796	0.895	0.496	0.740
2,4-DNT	0.118	0.112	2.25	2.25	0.977	1.87
3,5-DNT	<d	<d	0.290	0.266	<d	0.231
1,3,5-TNB	<d	<d	0.048	<d	<d	0.044
2,4,6-TNT	<d	<d	0.033	0.029	0.019	0.033
110 days						
1,3-DNB	not done	<d	not done	33.4	not done	32.0
1,2-DNB		0.139		3.57		3.28
2,5-DNT		<d		1.73		1.57
2,4-DNT		0.119		6.19		5.89
3,5-DNT		<d		0.938		0.871
1,3,5-TNB		<d		<d		<d
2,4,6-TNT		<d		<d		<d
173 days						
1,3-DNB	not done	<d	not done	not done	not done	not done
1,2-DNB		0.316				
2,5-DNT		<d				
2,4-DNT		0.046				
3,5-DNT		<d				
1,3,5-TNB		<d				
2,4,6-TNT		0.036				

<d Values were less than the detection limit.

Table A4. Analyte mass collected (pg/min) in headspace vapor above silt containing buried U.S. military-grade TNT, at 23°C, and three moisture levels.

	Air dry		*5.8% moisture*		*10% moisture*	
Sample	*Rep A*	*Rep B*	*Rep A*	*Rep B*	*Rep A*	*Rep B*
6 days						
1,3-DNB	<d	<d	59.4	64.9	49.7	51.4
1,2-DNB	<d	<d	8.80	50.5	8.40	8.44
2,5-DNT	<d	<d	2.50	15.6	1.91	1.85
2,4-DNT	0.145	0.274	49.7	131	51.4	51.3
3,5-DNT	<d	<d	15.8	27.2	15.4	15.0
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	0.652	0.807	1.59	1.71	1.54	1.83
15 days						
1,3-DNB	<d	0.861	72.1	81.8	79.7	not done
1,2-DNB	<d	0.220	9.28	8.38	10.9	
2,5-DNT	<d	0.088	0.886	1.01	1.28	
2,4-DNT	0.132	2.25	125	141	150	
3,5-DNT	<d	0.626	20.0	20.8	23.4	
1,3,5-TNB	<d	0.169	<d	0.204	<d	
2,4,6-TNT	0.079	0.622	1.36	1.18	1.96	
22 days						
1,3-DNB	<d	<d	75.7	120	69.6	91.7
1,2-DNB	<d	<d	8.36	11.4	10.6	12.6
2,5-DNT	<d	<d	<d	0.969	0.970	1.31
2,4-DNT	0.202	0.144	137	207	148	191
3,5-DNT	<d	<d	<d	32.1	25.0	31.1
1,3,5-TNB	<d	<d	0.201	0.217	0.175	0.212
2,4,6-TNT	0.146	0.077	1.34	2.08	7.17	5.34
34 days						
1,3-DNB	0.169	<d	126	95.3	69.8	103
1,2-DNB	0.118	0.209	11.7	10.3	10.9	14.3
2,5-DNT	<d	<d	0.841	0.662	1.05	1.43
2,4-DNT	0.296	0.255	252	213	166	243
3,5-DNT	<d	<d	39.9	<d	29.3	40.7
1,3,5-TNB	<d	<d	0.364	0.361	0.251	0.185
2,4,6-TNT	0.415	0.197	4.69	5.07	14.9	17.3
63 days						
1,3-DNB	0.172	<d	129	112	99.6	100
1,2-DNB	0.210	0.228	12.0	10.7	14.3	14.1
2,5-DNT	0.044	<d	0.732	0.643	1.64	1.40
2,4-DNT	0.376	0.140	255	223	204	214
3,5-DNT	0.175	<d	38.6	34.8	33.9	34.2
1,3,5-TNB	<d	<d	0.144	0.236	1.44	1.97
2,4,6-TNT	1.11	0.567	5.22	6.52	19.4	20.2
112 days						
1,3-DNB	not done	<d	not done	66.6	not done	61.0
1,2-DNB		0.125		7.20		9.35
2,5-DNT		<d		0.485		1.06
2,4-DNT		0.126		130		131
3,5-DNT		<d		22.7		23.3
1,3,5-TNB		<d		0.891		3.15
2,4,6-TNT		<d		6.10		20.2
173 days						
1,3-DNB	not done	0.056	not done	not done	not done	not done
1,2-DNB		0.042				
2,5-DNT		<d				
2,4-DNT		0.066				
3,5-DNT		<d				
1,3,5-TNB		0.048				
2,4,6-TNT		0.040				

<d Values were less than the detection limit.

To Contents

Table A5. Analyte mass collected (pg/min) in headspace vapor above silt containing buried U.S. military-grade TNT, at 4°C, and three moisture levels.

	Air dry		*5.8% moisture*		*10% moisture*	
Sample	*Rep A*	*Rep B*	*Rep A*	*Rep B*	*Rep A*	*Rep B*
12 days						
1,3-DNB	<d	<d	7.41	4.21	4.89	8.24
1,2-DNB	<d	<d	1.56	0.848	1.06	1.69
2,5-DNT	<d	<d	0.517	0.182	0.277	0.612
2,4-DNT	0.296	0.267	3.43	1.55	2.57	4.54
3,5-DNT	<d	<d	0.908	0.674	0.557	1.12
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	0.577	0.453	0.542	2.18	0.990	1.37
19 days						
1,3-DNB	<d	<d	9.56	not done	6.04	21.6
1,2-DNB	<d	<d	1.99		1.30	4.44
2,5-DNT	<d	<d	0.480		0.325	1.27
2,4-DNT	0.193	0.125	8.09		6.15	20.4
3,5-DNT	<d	<d	1.68		1.29	3.90
1,3,5-TNB	<d	<d	<d		<d	<d
2,4,6-TNT	<d	0.480	0.108		0.210	0.617
35 days						
1,3-DNB	<d	<d	51.0	31.7	27.6	32.4
1,2-DNB	<d	<d	10.6	5.25	5.02	7.26
2,5-DNT	<d	<d	2.60	0.754	1.46	2.11
2,4-DNT	0.122	0.112	51.3	27.1	31.9	42.7
3,5-DNT	<d	<d	9.89	5.04	6.22	<d
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	<d	0.638	0.655	0.604	0.341
67 days						
1,3-DNB	<d	<d	57.6	49.5	38.9	43.2
1,2-DNB	0.036	0.027	10.6	8.48	6.68	8.12
2,5-DNT	<d	<d	2.40	1.53	1.52	2.00
2,4-DNT	0.203	0.116	60.5	47.1	43.4	53.0
3,5-DNT	0.068	<d	11.0	8.67	8.00	9.65
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	0.044	<d	0.604	0.562	1.25	1.09
111 days						
1,3-DNB	not done	<d	not done	40.0	not done	32.4
1,2-DNB		<d		6.42		5.65
2,5-DNT		<d		1.23		1.57
2,4-DNT		0.168		42.2		43.8
3,5-DNT		<d		7.88		<d
1,3,5-TNB		<d		<d		<d
2,4,6-TNT		<d		0.411		0.757
173 days						
1,3-DNB	not done	<d	not done	not done	not done	not done
1,2-DNB		<d				
2,5-DNT		<d				
2,4-DNT		0.053				
3,5-DNT		<d				
1,3,5-TNB		<d				
2,4,6-TNT		0.025				
2,4,6-TNT		0.096				

<d Values were less than the detection limit.

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Table A6. Analyte mass collected (pg/min) in headspace vapor above silt containing buried U.S. military-grade TNT, at –12°C, and three moisture levels.

	Air dry		*2.1% moisture*		*3.1% moisture*	
Sample	*Rep A*	*Rep B*	*Rep A*	*Rep B*	*Rep A*	*Rep B*
13 days						
1,3-DNB	<d	<d	<d	<d	<d	<d
1,2-DNB	<d	<d	<d	<d	<d	<d
2,5-DNT	<d	<d	<d	<d	<d	<d
2,4-DNT	0.072	0.063	0.487	0.440	0.306	0.219
3,5-DNT	<d	<d	<d	<d	<d	<d
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	<d	<d	<d	<d	<d
20 days						
1,3-DNB	<d	<d	<d	<d	<d	<d
1,2-DNB	<d	<d	<d	<d	<d	<d
2,5-DNT	<d	<d	<d	<d	<d	<d
2,4-DNT	0.245	0.127	0.193	0.089	0.212	0.095
3,5-DNT	<d	<d	<d	<d	<d	<d
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	<d	<d	<d	<d	<d
36 days						
1,3-DNB	<d	<d	4.360	4.22	1.53	3.56
1,2-DNB	<d	<d	0.446	0.42	0.158	0.339
2,5-DNT	<d	<d	0.197	0.192	0.075	0.159
2,4-DNT	0.206	0.199	0.169	0.209	0.199	0.199
3,5-DNT	<d	<d	<d	<d	<d	<d
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	<d	<d	<d	<d	<d
69 days						
1,3-DNB	<d	<d	16.9	19.1	12.1	16.3
1,2-DNB	<d	<d	1.74	1.87	1.17	1.54
2,5-DNT	<d	<d	0.796	0.895	0.496	0.74
2,4-DNT	0.118	0.112	2.250	2.250	0.977	1.870
3,5-DNT	<d	<d	0.29	0.266	<d	0.231
1,3,5-TNB	<d	<d	0.048	<d	<d	0.044
2,4,6-TNT	<d	<d	0.033	0.029	0.019	0.033
110 days						
1,3-DNB	not done	<d	not done	33.4	not done	32
1,2-DNB		0.139		3.570		3.28
2,5-DNT		<d		1.73		1.57
2,4-DNT		0.119		6.190		5.890
3,5-DNT		<d		0.938		0.871
1,3,5-TNB		<d		<d		<d
2,4,6-TNT		<d		<d		<d
173 days						
1,3-DNB	not done	<d	not done	not done	not done	not done
1,2-DNB		0.316				
2,5-DNT		<d				
2,4-DNT		0.046				
3,5-DNT		<d				
1,3,5-TNB		<d				
2,4,6-TNT		0.036				

<d Values were less than the detection limit.

To Contents

Table A7. Analyte mass collected (pg/min) in headspace vapor above clay containing buried U.S. military-grade TNT, at 23°C, and three moisture levels.

	Air dry		*15% moisture*		*30% moisture*	
Sample	*Rep A*	*Rep B*	*Rep A*	*Rep B*	*Rep A*	*Rep B*
6 days						
1,3-DNB	<d	<d	2.34	2.24	2.29	1.64
1,2-DNB	<d	<d	1.19	1.31	1.22	1.00
2,5-DNT	<d	<d	<d	0.054	<d	<d
2,4-DNT	<d	<d	<d	<d	<d	<d
3,5-DNT	<d	<d	21.8	23.2	19.8	15.8
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	<d	<d	<d	<d	<d
15 days						
1,3-DNB	<d	not done	7.31	not done	5.11	not done
1,2-DNB	<d		1.40		0.950	
2,5-DNT	<d		0.370		0.140	
2,4-DNT	<d		7.76		4.47	
3,5-DNT	<d		3.73		0.933	
1,3,5-TNB	<d		0.511		0.208	
2,4,6-TNT	<d		1.02		0.806	
22 days						
1,3-DNB	<d	<d	6.55	8.44	6.26	7.49
1,2-DNB	<d	<d	0.937	1.46	0.916	1.30
2,5-DNT	<d	<d	<d	0.333	0.148	0.368
2,4-DNT	<d	<d	13.4	18.5	10.5	14.2
3,5-DNT	<d	<d	<d	3.06	1.17	2.95
1,3,5-TNB	<d	<d	0.234	0.578	0.228	0.576
2,4,6-TNT	<d	<d	0.563	0.800	0.543	0.810
34 days						
1,3-DNB	<d	<d	10.0	9.98	8.85	7.63
1,2-DNB	<d	<d	1.22	1.64	1.45	0.909
2,5-DNT	<d	<d	0.146	0.216	0.290	0.123
2,4-DNT	<d	<d	36.4	36.0	29.0	25.2
3,5-DNT	<d	<d	3.73	3.86	3.06	2.55
1,3,5-TNB	<d	<d	0.606	0.168	0.912	0.386
2,4,6-TNT	<d	<d	0.477	0.473	0.424	0.328
63 days						
1,3-DNB	<d	<d	5.48	6.32	4.50	5.22
1,2-DNB	<d	<d	1.05	1.13	0.901	1.05
2,5-DNT	<d	<d	0.076	0.049	0.064	0.057
2,4-DNT	<d	<d	25.9	28.6	19.6	24.1
3,5-DNT	<d	<d	2.77	3.09	2.13	2.60
1,3,5-TNB	<d	<d	0.436	0.457	0.433	0.456
2,4,6-TNT	<d	<d	0.287	0.303	0.211	0.262
112 days						
1,3-DNB	not done	<d	not done	7.24	not done	6.17
1,2-DNB		<d		1.71		1.53
2,5-DNT		<d		0.055		0.057
2,4-DNT		<d		40.4		33.6
3,5-DNT		<d		5.13		4.27
1,3,5-TNB		<d		0.716		0.711
2,4,6-TNT		<d		0.550		0.531
173 days						
1,3-DNB	not done	<d	not done	not done	not done	not done
1,2-DNB		<d				
2,5-DNT		<d				
2,4-DNT		0.043				
3,5-DNT		<d				
1,3,5-TNB		<d				
2,4,6-TNT		0.016				

<d Values were less than the detection limit.

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Table A8. Analyte mass collected (pg/min) in headspace vapor above clay containing buried U.S. military-grade TNT, at 4°C, and three moisture levels.

	Air dry		*15% moisture*		*30% moisture*	
Sample	*Rep A*	*Rep B*	*Rep A*	*Rep B*	*Rep A*	*Rep B*
12 days						
1,3-DNB	<d	<d	<d	<d	<d	not done
1,2-DNB	<d	<d	<d	<d	<d	
2,5-DNT	<d	<d	<d	<d	<d	
2,4-DNT	<d	<d	4.77	2.39	3.77	
3,5-DNT	<d	<d	<d	<d	<d	
1,3,5-TNB	<d	<d	<d	<d	<d	
2,4,6-TNT	<d	<d	<d	<d	<d	
19 days						
1,3-DNB	<d	<d	<d	0.324	0.291	0.397
1,2-DNB	<d	<d	0.100	0.251	0.115	0.195
2,5-DNT	<d	<d	<d	<d	<d	<d
2,4-DNT	0.130	0.123	0.161	0.213	0.226	0.336
3,5-DNT	<d	<d	<d	<d	<d	<d
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	<d	<d	<d	<d	<d
35 days						
1,3-DNB	<d	<d	1.86	2.45	3.73	1.78
1,2-DNB	<d	<d	0.533	0.794	0.909	0.465
2,5-DNT	<d	<d	<d	<d	<d	<d
2,4-DNT	0.109	0.167	0.293	0.329	2.11	1.04
3,5-DNT	<d	<d	0.235	0.209	0.331	0.377
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	<d	<d	<d	<d	<d
67 days						
1,3-DNB	<d	<d	4.05	5.57	2.54	1.33
1,2-DNB	<d	<d	0.596	0.930	0.708	0.384
2,5-DNT	<d	<d	<d	0.029	0.050	<d
2,4-DNT	0.172	0.128	1.74	2.15	6.81	4.18
3,5-DNT	<d	<d	0.494	0.574	0.932	0.535
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	<d	<d	0.028	0.042	0.032
111 days						
1,3-DNB	not done	<d	not done	5.74	not done	0.430
1,2-DNB		<d		0.725		0.303
2,5-DNT		<d		0.039		0.035
2,4-DNT		<d		4.52		5.07
3,5-DNT		<d		0.609		0.565
1,3,5-TNB		<d		<d		<d
2,4,6-TNT		<d		0.057		0.069
173 days						
1,3-DNB	not done	<d	not done	not done	not done	not done
1,2-DNB		<d				
2,5-DNT		<d				
2,4-DNT		0.044				
3,5-DNT		<d				
1,3,5-TNB		<d				
2,4,6-TNT		0.016				

<d Values were less than the detection limit.

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Table A9. Analyte mass (pg/min) collected in headspace vapor above clay containing buried U.S. military-grade TNT, at –12°C, and three moisture levels.

	Air dry		*15% moisture*		*30% moisture*	
Sample	*Rep A*	*Rep B*	*Rep A*	*Rep B*	*Rep A*	*Rep B*
13 days						
1,3-DNB	<d	<d	<d	<d	<d	<d
1,2-DNB	<d	<d	<d	<d	<d	<d
2,5-DNT	<d	<d	<d	<d	<d	<d
2,4-DNT	<d	<d	<d	<d	<d	<d
3,5-DNT	<d	<d	<d	<d	<d	<d
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	<d	<d	<d	<d	<d
20 days						
1,3-DNB	<d	<d	<d	<d	<d	<d
1,2-DNB	<d	<d	<d	<d	<d	<d
2,5-DNT	<d	<d	<d	<d	<d	<d
2,4-DNT	<d	<d	<d	<d	<d	<d
3,5-DNT	<d	<d	<d	<d	<d	<d
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	<d	<d	<d	<d	<d
36 days						
1,3-DNB	<d	<d	<d	<d	<d	<d
1,2-DNB	<d	<d	<d	<d	<d	<d
2,5-DNT	<d	<d	<d	<d	<d	<d
2,4-DNT	<d	<d	<d	<d	<d	<d
3,5-DNT	<d	<d	<d	<d	<d	<d
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	<d	<d	<d	<d	<d
69 days						
1,3-DNB	<d	<d	<d	<d	<d	<d
1,2-DNB	<d	<d	<d	<d	<d	<d
2,5-DNT	<d	<d	<d	<d	<d	<d
2,4-DNT	<d	<d	<d	<d	<d	<d
3,5-DNT	<d	<d	<d	<d	<d	<d
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	<d	<d	<d	<d	<d
110 days						
1,3-DNB	not done	<d	not done	<d	not done	<d
1,2-DNB		<d		<d		<d
2,5-DNT		<d		<d		<d
2,4-DNT		<d		<d		<d
3,5-DNT		<d		<d		<d
1,3,5-TNB		<d		<d		<d
2,4,6-TNT		<d		<d		<d
173 days						
1,3-DNB	not done	<d	not done	<d	not done	0.072
1,2-DNB		<d		<d		0.021
2,5-DNT		<d		<d		<d
2,4-DNT		0.043		0.116		0.094
3,5-DNT		<d		<d		<d
1,3,5-TNB		<d		0.026		0.036
2,4,6-TNT		0.011		0.245		0.107

<d Values were less than the detection limit.

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Table A10. Analyte concentration (pg/mL) in headspace vapor above sand containing buried U.S. military-grade TNT, at 23°C, and three moisture levels.

	Air dry		*2.1% moisture*		*3.1% moisture*	
Sample	*Rep A*	*Rep B*	*Rep A*	*Rep B*	*Rep A*	*Rep B*
6-days						
1,3-DNB	6.82	9.59	130	101	66.3	67.1
1,2-DNB	3.84	4.90	24.6	18.4	13.5	13.9
2,5-DNT	0.544	<d	14.3	<d	8.35	8.82
2,4-DNT	0.525	0.874	168	133	98.0	111
3,5-DNT	<d	<d	40.7	<d	25.1	27.8
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	0.116	0.133	9.04	6.47	5.96	14.3
15 days						
1,3-DNB	58.5	172	275	66.4	54.3	121
1,2-DNB	18.9	42.2	53.1	14.8	13.4	24.2
2,5-DNT	4.68	12.8	26.7	4.84	4.42	11.5
2,4-DNT	26.2	6.88	**>280**	125	116	228
3,5-DNT	2.44	6.25	86.1	25.1	23.6	44.9
1,3,5-TNB	<d	<d	1.70	1.98	1.40	0.947
2,4,6-TNT	3.18	3.65	30.1	17.5	14.3	24.0
22 days						
1,3-DNB	12.3	17.7	not done	267	62.9	151
1,2-DNB	6.28	8.76		43.1	15.1	29.7
2,5-DNT	0.856	0.072		15.0	4.38	11.8
2,4-DNT	5.17	7.29		**>306**	134	282
3,5-DNT	0.580	0.817		77.6	27.2	<d
1,3,5-TNB	<d	<d		17.2	2.69	2.09
2,4,6-TNT	0.509	0.443		30.8	29.6	51.1
34 days						
1,3-DNB	54.7	74.8	126	288	217	74.3
1,2-DNB	19.2	25.4	29.4	49.9	42.6	17.1
2,5-DNT	4.42	5.51	11.3	17.9	15.9	5.48
2,4-DNT	42.1	45.0	253	**>343**	**>343**	176
3,5-DNT	6.06	<d	56.7	99.6	83.4	37.0
1,3,5-TNB	<d	<d	24.2	8.89	6.54	10.9
2,4,6-TNT	7.72	6.07	153	140	123	171
63 days						
1,3-DNB	68.6	64.3	419	276	233	191
1,2-DNB	22.9	21.3	77.7	50.2	45.5	34.5
2,5-DNT	4.93	4.56	35.1	17.2	16.2	12.8
2,4-DNT	35.8	33.9	**>211**	125	**>211**	**>211**
3,5-DNT	4.63	4.48	122	331	76.5	64.9
1,3,5-TNB	<d	<d	13.9	9.08	7.84	5.18
2,4,6-TNT	3.15	3.22	89.4	112	107	86.5
112 days						
1,3-DNB	not done	5.86	not done	401	not done	231
1,2-DNB		3.58		76.3		44.9
2,5-DNT		0.407		25.2		16.6
2,4-DNT		1.93		604		427
3,5-DNT		0.267		125		85.6
1,3,5-TNB		<d		8.59		2.96
2,4,6-TNT		0.542		134.7		97.7

<d Values were less than the detection limit.

>bold Value greater than detector maximum signal.

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Table A11. Analyte concentration (pg/mL) in headspace vapor above sand containing buried U.S. military-grade TNT, at 4°C, and three moisture levels.

	Air dry		*2.1% moisture*		*3.1% moisture*	
Sample	*Rep A*	*Rep B*	*Rep A*	*Rep B*	*Rep A*	*Rep B*
12 days						
1,3-DNB	<d	<d	3.19	10.9	6.57	6.21
1,2-DNB	0.031	0.014	0.725	2.24	1.42	1.42
2,5-DNT	<d	<d	0.461	1.63	0.987	1.02
2,4-DNT	0.184	0.080	3.63	10.6	7.06	6.58
3,5-DNT	<d	<d	1.09	3.36	2.05	1.94
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	0.429	0.313	0.870	1.09	3.09	0.739
19 days						
1,3-DNB	0.036	<d	40.5	26.7	6.17	18.7
1,2-DNB	0.008	<d	7.05	5.94	1.45	4.34
2,5-DNT	0.017	<d	4.35	2.93	0.613	2.17
2,4-DNT	0.169	0.034	49.2	40.6	10.6	31.9
3,5-DNT	0.030	0.031	9.85	8.80	2.46	7.01
1,3,5-TNB	0.063	<d	<d	0.082	0.071	0.070
2,4,6-TNT	1.87	0.034	1.12	2.03	3.20	1.91
35 days						
1,3-DNB	<d	<d	56.3	34.7	27.7	32.9
1,2-DNB	<d	<d	10.9	8.31	6.29	6.88
2,5-DNT	<d	<d	6.33	3.96	2.79	3.82
2,4-DNT	0.033	0.027	78.6	60.6	47.5	52.8
3,5-DNT	<d	<d	16.0	13.4	10.7	0
1,3,5-TNB	<d	<d	0.098	0.388	0.300	0.198
2,4,6-TNT	0.044	0.022	2.79	5.64	7.71	5.01
67 days						
1,3-DNB	<d	<d	38.1	43.1	28.5	35.9
1,2-DNB	<d	<d	8.49	9.90	5.75	8.25
2,5-DNT	<d	<d	4.69	5.74	3.23	4.63
2,4-DNT	0.031	0.029	60.8	71.3	44.1	61.1
3,5-DNT	<d	<d	11.6	14.4	8.57	12.3
1,3,5-TNB	<d	<d	0.075	0.130	0.069	0.156
2,4,6-TNT	0.013	0.007	1.66	3.80	2.28	5.11
111 days						
1,3-DNB	not done	<d	not done	47.8	not done	31.8
1,2-DNB		<d		10.6		7.19
2,5-DNT		<d		6.36		4.15
2,4-DNT		0.018		82.0		56.5
3,5-DNT		<d		16.7		11.4
1,3,5-TNB		<d		<d		<d
2,4,6-TNT		0.006292685		2.28		1.61
173 days						
1,3DNB	not done	<d	not done	not done	not done	not done
1,2-DNB		0.080				
2,5-DNT		<d				
2,4-DNT		0.020				
3,5-DNT		<d				
1,3,5-TNB		0.010				
2,4,6-TNT		0.042				

<d Values were less than the detection limit

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Table A12. Analyte concentration (pg/mL) in headspace vapor above sand containing buried U.S. military-grade TNT, at –12°C, and three moisture levels.

	Air dry		*2.1% moisture*		*3.1% moisture*	
Sample	*Rep A*	*Rep B*	*Rep A*	*Rep B*	*Rep A*	*Rep B*
13 days						
1,3-DNB	<d	<d	<d	<d	<d	<d
1,2-DNB	<d	<d	<d	<d	<d	<d
2,5-DNT	<d	<d	<d	<d	<d	<d
2,4-DNT	0.016	0.014	0.108	0.098	0.068	0.049
3,5-DNT	<d	<d	<d	<d	<d	<d
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	<d	<d	<d	<d	<d
20 days						
1,3-DNB	<d	<d	<d	<d	<d	<d
1,2-DNB	<d	<d	<d	<d	<d	<d
2,5-DNT	<d	<d	<d	<d	<d	<d
2,4-DNT	0.055	0.028	0.043	0.020	0.047	0.021
3,5-DNT	<d	<d	<d	<d	<d	<d
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	<d	<d	<d	<d	<d
36 days						
1,3-DNB	<d	<d	1.02	0.981	0.355	0.829
1,2-DNB	<d	<d	0.104	0.098	0.037	0.079
2,5-DNT	<d	<d	0.046	0.045	0.017	0.037
2,4-DNT	0.046	0.044	0.038	0.046	0.044	0.044
3,5-DNT	<d	<d	<d	<d	<d	<d
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	<d	<d	<d	<d	<d
69 days						
1,3-DNB	<d	<d	3.92	4.45	2.81	3.78
1,2-DNB	<d	<d	0.406	0.434	0.273	0.359
2,5-DNT	<d	<d	0.185	0.208	0.115	0.172
2,4-DNT	0.026	0.025	0.501	0.500	0.217	0.415
3,5-DNT	<d	<d	0.067	0.062	<d	0.054
1,3,5-TNB	<d	<d	0.021	<d	<d	0.019
2,4,6-TNT	<d	<d	0.014	0.013	0.008	0.014
110 days						
1,3-DNB	not done	<d	not done	7.76	not done	7.43
1,2-DNB		0.032		0.831		0.764
2,5-DNT		<d		0.403		0.365
2,4-DNT		0.026		1.38		1.31
3,5-DNT		<d		0.218		0.203
1,3,5-TNB		<d		<d		<d
2,4,6-TNT		<d		<d		<d
173 days						
1,3-DNB	not done	<d	not done	not done	not done	not done
1,2-DNB		0.074				
2,5-DNT		<d				
2,4-DNT		0.010				
3,5-DNT		<d				
1,3,5-TNB		<d				
2,4,6-TNT		0.016				

<d Values were less than the detection limit.

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Table A13. Analyte concentration (pg/mL) in headspace vapor above silt containing buried U.S. military-grade TNT, at 23°C, and three moisture levels.

	Air dry		*5.8% moisture*		*10% moisture*	
Sample	*Rep A*	*Rep B*	*Rep A*	*Rep B*	*Rep A*	*Rep B*
6 days						
1,3-DNB	<d	<d	13.8	15.1	11.6	12.0
1,2-DNB	<d	<d	2.05	11.7	1.95	1.96
2,5-DNT	<d	<d	0.580	3.63	0.444	0.431
2,4-DNT	0.032	0.061	11.0	29.1	11.4	11.4
3,5-DNT	<d	<d	3.67	6.33	3.57	3.49
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	0.283	0.351	0.690	0.743	0.668	0.794
15 days						
1,3-DNB	<d	0.200	16.8	19.0	18.5	not done
1,2-DNB	<d	0.051	2.16	1.95	2.54	
2,5-DNT	<d	0.021	0.206	0.234	0.297	
2,4-DNT	0.029	0.499	27.7	31.2	33.4	
3,5-DNT	<d	0.146	4.64	4.83	5.44	
1,3,5-TNB	<d	0.073	0	0.089	0	
2,4,6-TNT	0.034	0.271	0.592	0.515	0.854	
22 days						
1,3-DNB	<d	<d	17.6	27.9	16.2	21.3
1,2-DNB	<d	<d	1.94	2.66	2.46	2.93
2,5-DNT	<d	<d	0	0.225	0.225	0.305
2,4-DNT	0.045	0.032	30.5	46.1	33.0	42.5
3,5-DNT	<d	<d	0	7.47	5.81	7.24
1,3,5-TNB	<d	<d	0.088	0.094	0.076	0.092
2,4,6-TNT	0.063	0.033	0.584	0.902	3.12	2.32
34 days						
1,3-DNB	0.039	<d	29.3	22.2	16.2	23.9
1,2-DNB	0.028	0.049	2.72	2.40	2.52	3.32
2,5-DNT	<d	<d	0.195	0.154	0.243	0.332
2,4-DNT	0.066	0.057	56.0	47.2	36.9	54.0
3,5-DNT	<d	<d	9.28	0	6.81	9.48
1,3,5-TNB	<d	<d	0.158	0.157	0.109	0.080
2,4,6-TNT	0.180	0.086	2.04	2.21	6.47	7.51
63 days						
1,3-DNB	0.040	<d	30.0	26.0	23.2	23.3
1,2-DNB	0.049	0.053	2.79	2.48	3.32	3.29
2,5-DNT	0.010	<d	0.170	0.150	0.382	0.325
2,4-DNT	0.083	0.031	56.7	49.6	45.4	47.5
3,5-DNT	0.041	<d	8.98	8.10	7.88	7.96
1,3,5-TNB	<d	<d	0.063	0.103	0.624	0.855
2,4,6-TNT	0.482	0.247	2.27	2.83	8.46	8.79
112 days						
1,3-DNB	not done	<d	not done	15.5	not done	14.2
1,2-DNB		0.029		1.67		2.17
2,5-DNT		<d		0.113		0.245
2,4-DNT		0.028		28.9		29.1
3,5-DNT		<d		5.28		5.42
1,3,5-TNB		<d		0.388		1.37
2,4,6-TNT		<d		2.65		8.77
173 days						
1,3-DNB	not done	0.013	not done	not done	not done	not done
1,2-DNB		0.010				
2,5-DNT		<d				
2,4-DNT		0.015				
3,5-DNT		<d				
1,3,5-TNB		0.021				
2,4,6-TNT		0.017				

<d Values were less than the detection limit.

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Table A14. Analyte concentration (pg/mL) in headspace vapor above silt containing buried U.S. military-grade TNT, at 4°C, and three moisture levels.

	Air dry		*5.8% moisture*		*10% moisture*	
Sample	*Rep A*	*Rep B*	*Rep A*	*Rep B*	*Rep A*	*Rep B*
12 days						
1,3-DNB	<d	<d	1.72	0.978	1.14	1.92
1,2-DNB	<d	<d	0.364	0.197	0.247	0.393
2,5-DNT	<d	<d	0.120	0.042	0.064	0.142
2,4-DNT	0.066	0.059	0.761	0.346	0.572	1.01
3,5-DNT	<d	<d	0.211	0.157	0.130	0.260
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	0.251	0.197	0.236	0.950	0.431	0.598
19 days						
1,3-DNB	<d	<d	2.22	not done	1.40	5.03
1,2-DNB	<d	<d	0.463		0.302	1.03
2,5-DNT	<d	<d	0.112		0.076	0.296
2,4-DNT	0.043	0.028	1.80		1.37	4.53
3,5-DNT	<d	<d	0.390		0.299	0.908
1,3,5-TNB	<d	<d	<d		<d	<d
2,4,6-TNT	<d	0.209	0.047		0.091	0.268
35 days						
1,3-DNB	<d	<d	11.8	7.37	6.41	7.53
1,2-DNB	<d	<d	2.47	1.22	1.17	1.69
2,5-DNT	<d	<d	0.604	0.175	0.340	0.491
2,4-DNT	0.027	0.025	11.4	6.02	7.09	9.48
3,5-DNT	<d	<d	2.30	1.17	1.45	<d
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	<d	0.278	0.285	0.263	0.148
67 days						
1,3-DNB	<d	<d	13.4	11.5	9.05	10.0
1,2-DNB	0.008	0.006	2.47	1.97	1.55	1.89
2,5-DNT	<d	<d	0.559	0.356	0.353	0.466
2,4-DNT	0.045	0.026	13.4	10.5	9.64	11.8
3,5-DNT	0.016	<d	2.57	2.02	1.86	2.25
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	0.019	<d	0.263	0.244	0.543	0.474
111 days						
1,3-DNB	not done	<d	not done	9.29	not done	7.53
1,2-DNB		<d		1.49		1.31
2,5-DNT		<d		0.287		0.364
2,4-DNT		0.037		9.38		9.72
3,5-DNT		<d		1.83		<d
1,3,5-TNB		<d		<d		<d
2,4,6-TNT		<d		0.179		0.329
173-days						
1,3-DNB	not done	<d	not done	not done	not done	not done
1,2-DNB		<d				
2,5-DNT		<d				
2,4-DNT		0.012				
3,5-DNT		<d				
1,3,5-TNB		<d				
2,4,6-TNT		0.011				

<d Values were less than the detection limit.

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Table A15. Analyte concentration (pg/mL) in headspace vapor above silt containing buried U.S. military-grade TNT, at –12°C, and three moisture levels.

	Air dry		*5.8% moisture*		*10% moisture*	
Sample	*Rep A*	*Rep B*	*Rep A*	*Rep B*	*Rep A*	*Rep B*
13 days						
1,3-DNB	<d	<d	<d	<d	<d	<d
1,2-DNB	<d	<d	<d	<d	<d	<d
2,5-DNT	<d	<d	<d	<d	<d	<d
2,4-DNT	0.046	0.032	0.047	0.029	0.043	0.013
3,5-DNT	<d	<d	<d	<d	<d	<d
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	<d	<d	<d	<d	<d
20 days						
1,3-DNB	<d	<d	<d	<d	<d	<d
1,2-DNB	<d	<d	<d	<d	<d	<d
2,5-DNT	<d	<d	<d	<d	<d	<d
2,4-DNT	0.058	0.020	0.025	0.062	0.027	0.031
3,5-DNT	<d	<d	<d	<d	<d	<d
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	<d	0.042	0.021	<d	<d
36 days						
1,3-DNB	<d	<d	0.038	<d	<d	<d
1,2-DNB	<d	<d	<d	<d	<d	<d
2,5-DNT	<d	<d	<d	<d	<d	<d
2,4-DNT	0.033	0.036	0.034	0.029	0.035	0.028
3,5-DNT	<d	<d	<d	<d	<d	<d
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	<d	0.048	<d	<d	<d
69 days						
1,3-DNB	<d	<d	<d	<d	<d	<d
1,2-DNB	<d	<d	<d	<d	<d	<d
2,5-DNT	<d	<d	<d	<d	<d	<d
2,4-DNT	0.025	0.029	0.021	0.020	0.034	0.034
3,5-DNT	<d	<d	<d	<d	<d	<d
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	<d	<d	<d	<d	<d
110 days						
1,3-DNB	not done	<d	not done	<d	not done	<d
1,2-DNB		<d		0.016		<d
2,5-DNT		<d		<d		<d
2,4-DNT		0.024		0.026		0.013
3,5-DNT		<d		<d		<d
1,3,5-TNB		<d		<d		<d
2,4,6-TNT		<d		<d		<d
173 days						
1,3-DNB	not done	<d	not done	0.168	not done	<d
1,2-DNB		<d		0.081		0.009
2,5-DNT		<d		<d		<d
2,4-DNT		0.037		0.018		0.010
3,5-DNT		<d		<d		<d
1,3,5-TNB		<d		<d		0.012
2,4,6-TNT		0.163		0.016		0.006

<d Values were less than the detection limit.

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Table A16. Analyte concentration (pg/mL) in headspace vapor above clay containing buried U.S. military-grade TNT, at 23°C, and three moisture levels.

	Air dry		*15% moisture*		*30% moisture*	
Sample	*Rep A*	*Rep B*	*Rep A*	*Rep B*	*Rep A*	*Rep B*
6 days						
1,3-DNB	<d	<d	0.544	0.522	0.532	0.381
1,2-DNB	<d	<d	0.276	0.304	0.283	0.234
2,5-DNT	<d	<d	<d	0.013	<d	<d
2,4-DNT	<d	<d	<d	<d	<d	<d
3,5-DNT	<d	<d	5.07	5.40	4.60	3.68
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	<d	<d	<d	<d	<d
15 days						
1,3-DNB	<d	not done	1.70	not done	1.19	not done
1,2-DNB	<d		0.326		0.221	
2,5-DNT	<d		0.086		0.033	
2,4-DNT	<d		1.72		0.994	
3,5-DNT	<d		0.867		0.217	
1,3,5-TNB	<d		0.222		0.091	
2,4,6-TNT	<d		0.442		0.351	
22 days						
1,3-DNB	<d	<d	1.52	1.96	1.46	1.74
1,2-DNB	<d	<d	0.218	0.339	0.213	0.302
2,5-DNT	<d	<d	<d	0.077	0.035	0.086
2,4-DNT	<d	<d	2.97	4.11	2.33	3.16
3,5-DNT	<d	<d	<d	0.711	0.272	0.686
1,3,5-TNB	<d	<d	0.102	0.251	0.099	0.250
2,4,6-TNT	<d	<d	0.245	0.348	0.236	0.352
34 days						
1,3-DNB	<d	<d	2.33	2.32	2.06	1.77
1,2-DNB	<d	<d	0.284	0.380	0.336	0.211
2,5-DNT	<d	<d	0.034	0.050	0.068	0.029
2,4-DNT	<d	<d	8.09	7.99	6.45	5.60
3,5-DNT	<d	<d	0.867	0.897	0.712	0.594
1,3,5-TNB	<d	<d	0.264	0.073	0.397	0.168
2,4,6-TNT	<d	<d	0.207	0.206	0.184	0.142
63 days						
1,3-DNB	<d	<d	1.27	1.47	1.05	1.21
1,2-DNB	<d	<d	0.245	0.263	0.210	0.245
2,5-DNT	<d	<d	0.018	0.012	0.015	0.013
2,4-DNT	<d	<d	5.75	6.35	4.36	5.36
3,5-DNT	<d	<d	0.644	0.719	0.495	0.606
1,3,5-TNB	<d	<d	0.190	0.199	0.188	0.198
2,4,6-TNT	<d	<d	0.125	0.132	0.092	0.114
112 days						
1,3-DNB	not done	<d	not done	1.68	not done	1.44
1,2-DNB		<d		0.398		0.355
2,5-DNT		<d		0.013		0.013
2,4-DNT		<d		8.98		7.46
3,5-DNT		<d		1.19		0.994
1,3,5-TNB		<d		0.311		0.309
2,4,6-TNT		<d		0.239		0.231
173 days						
1,3-DNB	not done	<d	not done	not done	not done	not done
1,2-DNB		<d				
2,5-DNT		<d				
2,4-DNT		0.009567427				
3,5-DNT		<d				
1,3,5-TNB		<d				
2,4,6-TNT		0.006760614				

<d Values were less than the detection limit.

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Table A17. Analyte concentration (pg/mL) in headspace vapor above clay containing buried U.S. military-grade TNT, at 4°C, and three moisture levels.

	Air dry		*15% moisture*		*30% moisture*	
Sample	*Rep A*	*Rep B*	*Rep A*	*Rep B*	*Rep A*	*Rep B*
12 days						
1,3-DNB	<d	<d	<d	<d	<d	not done
1,2-DNB	<d	<d	<d	<d	<d	
2,5-DNT	<d	<d	<d	<d	<d	
2,4-DNT	<d	<d	1.06	0.532	0.837	
3,5-DNT	<d	<d	<d	<d	<d	
1,3,5-TNB	<d	<d	<d	<d	<d	
2,4,6-TNT	<d	<d	<d	<d	<d	
19 days						
1,3-DNB	<d	<d	<d	0.075	0.068	0.092
1,2-DNB	<d	<d	0.023	0.058	0.027	0.045
2,5-DNT	<d	<d	<d	<d	<d	<d
2,4-DNT	0.029	0.027	0.036	0.047	0.050	0.075
3,5-DNT	<d	<d	<d	<d	<d	<d
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	<d	<d	<d	<d	<d
35 days						
1,3-DNB	<d	<d	0.434	0.569	0.867	0.413
1,2-DNB	<d	<d	0.124	0.185	0.211	0.108
2,5-DNT	<d	<d	<d	<d	<d	<d
2,4-DNT	0.024	0.037	0.065	0.073	0.470	0.232
3,5-DNT	<d	<d	0.055	0.049	0.077	0.088
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	<d	<d	<d	<d	<d
67 days						
1,3-DNB	<d	<d	0.941	1.30	0.591	0.310
1,2-DNB	<d	<d	0.139	0.216	0.165	0.089
2,5-DNT	<d	<d	<d	0.007	0.012	<d
2,4-DNT	0.038	0.029	0.386	0.477	1.51	0.929
3,5-DNT	<d	<d	0.115	0.134	0.217	0.124
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	<d	<d	0.012	0.018	0.014
111 days						
1,3-DNB	not done	<d	not done	1.34	not done	0.100
1,2-DNB		<d		0.169		0.070
2,5-DNT		<d		0.009		0.008
2,4-DNT		<d		1.00		1.13
3,5-DNT		<d		0.142		0.131
1,3,5-TNB		<d		<d		<d
2,4,6-TNT		<d		0.025		0.030
173 days						
1,3-DNB	not done	<d	not done	not done	not done	not done
1,2-DNB		<d				
2,5-DNT		<d				
2,4-DNT		0.010				
3,5-DNT		<d				
1,3,5-TNB		<d				
2,4,6-TNT		0.007				

<d Values were less than the detection limit.

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Table A18. Analyte concentration (pg/mL) in headspace vapor above clay containing buried U.S. military-grade TNT, at –12°C, and three moisture levels.

	Air dry		*15% moisture*		*30% moisture*	
Sample	*Rep A*	*Rep B*	*Rep A*	*Rep B*	*Rep A*	*Rep B*
13 days						
1,3-DNB	<d	<d	<d	<d	<d	<d
1,2-DNB	<d	<d	<d	<d	<d	<d
2,5-DNT	<d	<d	<d	<d	<d	<d
2,4-DNT	<d	<d	<d	<d	<d	<d
3,5-DNT	<d	<d	<d	<d	<d	<d
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	<d	<d	<d	<d	<d
20 days						
1,3-DNB	<d	<d	<d	<d	<d	<d
1,2-DNB	<d	<d	<d	<d	<d	<d
2,5-DNT	<d	<d	<d	<d	<d	<d
2,4-DNT	<d	<d	<d	<d	<d	<d
3,5-DNT	<d	<d	<d	<d	<d	<d
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	<d	<d	<d	<d	<d
36 days						
1,3-DNB	<d	<d	<d	<d	<d	<d
1,2-DNB	<d	<d	<d	<d	<d	<d
2,5-DNT	<d	<d	<d	<d	<d	<d
2,4-DNT	<d	<d	<d	<d	<d	<d
3,5-DNT	<d	<d	<d	<d	<d	<d
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	<d	<d	<d	<d	<d
69 days						
1,3-DNB	<d	<d	<d	<d	<d	<d
1,2-DNB	<d	<d	<d	<d	<d	<d
2,5-DNT	<d	<d	<d	<d	<d	<d
2,4-DNT	<d	<d	<d	<d	<d	<d
3,5-DNT	<d	<d	<d	<d	<d	<d
1,3,5-TNB	<d	<d	<d	<d	<d	<d
2,4,6-TNT	<d	<d	<d	<d	<d	<d
110 days						
1,3-DNB	not done	<d	not done	<d	not done	<d
1,2-DNB		<d		<d		<d
2,5-DNT		<d		<d		<d
2,4-DNT		<d		<d		<d
3,5-DNT		<d		<d		<d
1,3,5-TNB		<d		<d		<d
2,4,6-TNT		<d		<d		<d
173 days						
1,3-DNB	not done	<d	not done	<d	not done	0.017
1,2-DNB		<d		<d		0.005
2,5-DNT		<d		<d		<d
2,4-DNT		0.010		0.026		0.021
3,5-DNT		<d		<d		<d
1,3,5-TNB		<d		0.011		0.016
2,4,6-TNT		0.005		0.107		0.047

<d Values were less than the detection limit.

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14. ABSTRACT

Crystals of military-grade TNT were placed beneath 2.5 cm of soil in enclosed 40-mL amber vials and the accumulation of signature vapors in the headspace above the soil was determined as a function of time. Three different soils—sand, silt, and clay—were investigated at three different moisture contents: air dry, low moisture, and high moisture. Two replicates of each combination of soil type and soil moisture were equilibrated at three temperatures (23, 4 and −12°C) over periods ranging from 63 to 173 days.

The headspace was sampled by a polyacrylate solid phase microextraction (SPME) fiber for periods ranging from 5 to 20 minutes, and analytes were desorbed in the injection port of a gas chromatograph equipped with an electron capture detector. Mass detection limits using this method were below 1 pg (1×10^{-12} g) for the major signature chemicals—2,4-dinitrotoluene (2,4-DNT), 1,3-dinitrobenzene (1,3-DNB), and 2,4,6-trinitrotoluene (2,4,6-TNT). At the end of the experiment, the top 5 mm of soil was carefully removed, extracted with acetonitrile, and the extracts were analyzed using RP-HPLC-UV according to SW846 Method 8330.

15. SUBJECT TERMS

2,4-DNT	Explosives	Partition coefficients	TNT
Chemical detection	Headspace	SPME (solid phase microextraction)	Vapor signatures

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14. ABSTRACT (cont'd)

Both the qualitative and quantitative nature of the chemical signature above buried TNT is strongly a function of temperature. At 23 and 4°C, 2,4-DNT was present at the highest concentration in the headspace vapor, 2,4,6-TNT being only a minor component. At –12°C, the more volatile 1,3-DNB predominated. Vapors penetrate the soils in the order sand > silt > clay, with vapor concentrations in the same order. Dry soils are very retentive of TNT vapors, while soil moisture facilitates movement of vapors to the headspace.

Soil–air partition coefficients, computed for these three soils at 23 and 4°C for 2,4,6-TNT, ranged from 1.6×10^4 mL-air/g-soil for moist sand at 23°C to 3.0×10^7 for moist clay at 4°C. Partition coefficients for 2,4-DNT were about an order of magnitude lower. Vapor concentrations for several of the air-dried soils were too low to measure and hence the partition coefficients for dry soils could not be estimated, but were much higher than for the same soil with higher moisture. These results indicate that for detection of buried mines, the largest mass of signature chemicals will be present in the surface soil rather than the overlying air.

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